Preparation and Characterization of Cu-Cr Impregnated Silica Catalyst from Rice Husk

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This is to certify that, Swarnav Mitra, a student of M.Tech, 4th Semester, Chemical Engineering Department, NIT Rourkela bearing Roll No. 212CH1077 has completed his final project on the topic *"Preparation and Characterization of Cu-Cr Impregnated Silica Heterogeneous Catalyst from Rice Husk"* under my guidance successfully. He has shown an authentic work with valid results and submitted a complete thesis of the work as required according to the curriculum in partial fulfillment for the award of M. Tech. degree.

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Nomenclature

RH	Rice Husk
RHA	Rice Husk Ash
RSA	Rice Straw Ash
WWRH	Water Washed Rice Husk
AWRH	Acid Washed Rice Husk
WWRH-A	Water Washed Rice Husk – Ash
AWRH-A	Acid Washed Rice Husk – Ash
AWRHA-N	Acid Washed Rice Husk – N_2 atmosphere
CTAB	Cetyl Tetramethyl Ammonium Bromide
SDA	Structural Directing Agent
RhSi	Rice Husk Silica
RhSi-Cr/Cu	Rice Husk Silica Impregnated with Copper and Chromium
GC-MS	Gas Chromatography Mass Spectroscopy
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscope
EDX	Energy Dispersive X-ray
TGA	Thermogravimetric Analysis
BET	Brunauer–Emmett–Teller Surface Area Measurement
DFT	Discrete Fourier Transform surface Area Measurement
FTIR	Fourier Transform Infrared Spectroscopy
TEOS	Tetra Ethyl Ortho Silicate
TMOS	Tetra Methyl Ortho Silicate
PEDS	Poly Ethoxy Disiloxane
UNEP	United Nations Environment Programme
MCM	Mobil Composition of Matter

Abstract:

A simple method of alkaline extraction followed by acid precipitation of rice husk (RH) led to production of amorphous silica which was found to have high specific surface area and minimal mineral contaminants. In the present work pyrolysis and leaching with alkali helped to obtain amorphous silica with high surface area. Rice hulls were pyrolysed at different temperatures in a furnace and then treated with NaOH of various concentrations. The leachate were titrated with HCl to obtain silica. Acid leaching of the rice hulls prior to pyrolysis and then alkali treatment was also performed. Results thus obtained were compared with each other. X-ray diffraction of the silica helped to identify its amorphous nature. The removal of inorganic trace materials was observed after alkali treatment with ash obtained from acid treated RH. SEM and EDX studies were also performed on the silica and pyrolyzed RH. The amorphous nature and particle size were determined by SEM studies where presence of silica in pure form was confirmed. A controlled pyrolysis in N_2 atmosphere was also conducted to obtain white ash from which silica was further extracted using the same procedure i.e. alkaline extraction route as before followed by titration with dil. HNO_3 containing dissolved Chromium and Copper species. This gave rise to the metal impregnated silica catalysts from rice husk used as the source. The average surface area, pore diameter and total pore volume were obtained using N_2 adsorption desorption calculations by BET techniques. Micro-pore and meso-pore pore volume distribution were identified using DFT techniques for both the silica and metal modified silica. High surface areas above 250 m^2/g were observed with increase of pyrolysis temperature for the silica. Adsorption isotherm curves obtained were of type III. BET studies for the metal modified silica catalyst showed higher surface area. For the samples extracted at higher pH levels also type III isotherm curves were obtained. Thermogravimetric studies were also performed on the silica extracted from rice husk which was pyrolysed at 650, 750, 850 and 1000^oC. A four stage decrease in mass was observed with about 20% decrease in mass up to 800^oC. FTIR analysis of the catalyst thus obtained showed the presence of the silanol and siloxane bonds on the surface of silica. Presence of Si-O-Cr and Si-O-Cu bonds were also evident from the FTIR analysis. Strene was oxidised in a laboratory scale with the aid of the prepared catalysts. The oxidant used was H_2O_2 and acetonitrile was also used as a

solvent. The products thus formed were analyzed by GC-MS. The catalysts were found to give a good conversion of styrene to benzaldehyde with maximum conversion for catalyst samples extracted at lower pH. A comparison with the catalyst extracted at same pH but with higher metal (copper) content showed that the increase in copper content help to obtain better conversion and product selectivity. These studies finally help us to get a biogenic catalyst with high conversion and selectivity which can act as a heterogeneous catalyst on oxidation of styrene.

Keywords:

Rice Husk, Rice Husk Ash, Amorphous Silica, Metal Modified Silica Catalyst, Chromium-Copper Catalyst, SEM, XRD, TGA, BET, FTIR and GC-MS analysis.

CHAPTER 1

INTRODUCTION

1.1 Introduction - Overview

The population growth and its requirement for improvement of human living standards has led to huge increase in the amount of agricultural waste both in volume and in variety. Usually such waste is burned in open and when left in the open decomposes down elevating the disposal problem to higher extents. Decomposition and putrefaction emits methane and other obnoxious gases while burning produced gases which add to air pollution and also form ash as solid waste further increasing the pollution. Thus improper waste management adds to climate change, soil and water contamination and also aids air pollution.

If properly managed, waste agricultural biomass is of high worth because the energy that it contained in it is recovered. In parity with global organization surroundings findings (UNEP) findings, five billion metric a lot of biomass is generated each year from agriculture. Which is thermal equivalent to 2 billion a lot of oil, concerning a pair of 5% of current international production [1]

With growth of population there has been a massive increase in global energy demand and non-renewable sources are withering out at a fast rate. Use of carbon based fuel in the present world along with its increasing demand is not a sustainable source of energy as it results in CO_2 emission and effects the global climate. Development of alternative energy sources is the most worthy strategy to protect the global climate, reduction in use of nonrenewable fuel being the other. Processes to convert biomass into energy have been developed like gasification and use of biomass as fuel for boilers have been developed. Various techniques of conversion of biomass to energy and production of synthesis gas and generation of heat for various industrial processes have been reported in literature like biomass may be burnt in air, gasified, pyrolysed, fermented, digested or undergone mechanical extraction, with gasification being one of the most important and common method to obtain energy from burning and pyrolysing biomass and generating heat and synthesis gas. Pyrolysis or gasification of biomass results in the formation of char, which at times is formed in significant quantities and poses a serious disposal problem and causes environmental hazards. Various types of biomass give rise to different types of chars having varied properties. Characterizations of these types of chars have not been reported extensively.

Amorphous silica is known to be bioactive, biocompatible, biodegradable and non-toxic to the living human tissue, unlike silica in crystalline which induces adverse biological effects. In the present times amorphous silica along with fumed silica is increasingly used in biomedical applications, drug delivery and diagnostics. Potential silica based materials like, silica spheres, nano-spheres, mesoporous silica gel, silica aerogel, and silica star gel are used widely for and drug delivery and preparing artificial bone tissue. Since the discovery of silica-based bioactive glass by Hench in 1971 and then ordered mesoporous silica materials in the early 1990s' by scientists of the Mobil Corporation [2] and Waseda University [3], these materials lead to the development of a wide area of research on new silica-based bioactive materials for biomedical applications. In general, amorphous silica is prepared using silicon alkoxide raw materials. Tetra methyl ortho silicate (TMOS), tetra ethyl ortho silicate (TEOS) and poly ethoxy disiloxane (PEDS), etc are the commonly used alkoxides to prepare mesoporous amorphous silica. However, such precursors are fairly expensive. Thus alternative low cost amorphous silica precursors are required to substitute alkoxides. In that respect, a cheap source of amorphous silica of bio-origin would be the rice husk ash (RAH). Although RHA contains minor amount of other metallic impurities; it may be safely used in physiological environment as it is generated from biomass.

Rice husk ash/ char have been reported in many literatures to be used to derive silica in ultrapure amorphous form or simply in amorphous form. RHA is found to contain around 60% or more of silica thus making it useful as an economic raw material for production of silica gels and powders as reported by Kamath and Proctor [4] and also Chakraverty and Kaleemullah [5]. Rice husk has been used as a starting material to develop various silica substances like silica carbide, silicon nitride, silica itself in amorphous form and also elemental silicon. Leaching of rice husk with hot alkali results in formation of sodium silicate, which when treated with mineral acid gives us silica as precipitate. Primary treating of the rice husk prior to thermal treatment with mineral acids like HCl, H_2SO_4, HNO_3, have been reported in literature to remove impurities such as metals (found in traces) and producing white ash with high percentage of silica in it giving silica with high surface area. Biomass i.e. Rice husk is utilised for heat generation and drying in rice mills and has high calorific value. Rice husk is also used in gasification

plants to directly generate power or syn-gas. These burning, pyrolysis and gasification operations produce ash in relatively high amounts which also pose a disposal problem.

At present the most intense research work is going on in the area of ordered mesoporous silica for drug delivery and other biomedical applications. The important feature of mesoporous material is to host molecular size of particles within it. Silica aerogel is one such ordered mesoporous material and is also used in biomedical applications for controlled release of drugs, peptides, hormones, etc. [6]

In this work such ash i.e. pyrolysed rice husk ash has been characterized and silica has also been derived from the pyrolysed rice husk ash (RHA). This silica is found to be in amorphous format and was proven to have high surface area. This high surface area amorphous grade silica is impregnated with Copper and Chromium bi-metals and thus an oxidizing catalyst is developed. The prepared catalyst are used in oxidation of styrene and is converted to benzaldehyde which is compared with catalysts extracted at different pH conditions of the solution. Metal modified silica catalysts are prepared with two different metal containments, i.e. 5% and 10% (w/w) for Copper while the Chromium content was fixed at 10% (w/w). These metal modified catalyst are prepared at different solution conditions, i.e. in acidic, neutral and basic media, at pH of 3, 7 and 10 respectively. The oxidation of styrene to benzaldehyde is noted for all these catalysts and the best catalyst is then identified. Cetyl trimethyl ammonium bromide (CTAB) surfactant is used as a Structural Directing Agent (SDA) while incorporating the transition metals into the silica matrix. The SDA forms micelles and helps to maintain a particular size to the silica precursor while incorporating the metal into the matrix.

1.2. Rice Husk Ash and Extraction of Amorphous Silica

India produces about 120 million tons of paddy every year and along with it comes 24 million tons of rice husk which on burning would generate 4.4 tons of as (RHA). Rice husk ash is mostly used in steel, cement and refractory industries. Numerous examples of production of amorphous silica, silica nano particles, complex organo-silica matrixes and metal-silica compounds have been widely studied and reported in literature [7 - 10]. The process of obtaining rice from the paddy helps to obtain the husk which corresponds to 23% of the initial weight of the paddy. The ash from rice husk is highly

siliceous, containing 95-97% silica [5, 4]. Potassium, sodium, calcium, magnesium, iron, phosphorus and aluminium are the major impurities which occur in the form of oxides or silicates in RH. Samples obtained from various parts of the earth have been found to have different percentages of the above mentioned impurities, depending on the soil characteristics and the minerals available in it. The organic component of rice husk (RH) is around 72% of the husk by weight [11], remaining being silica. Silica after solubilizing produces soluble silicates. These silicates are widely used for the manufacture of glass, ceramics, and cement. A major portion is used in pharmaceuticals, cosmetics and detergents industries as bonding and abrasive agents. The dry basis analysis of rice husk has led to the finding that it contains 20% ash, 22% lignin, 38% cellulose, 18% pentosans, and 2% other organic matter. The husk surrounds the paddy grain as obtained from the crop. Milling of paddy helps to generates about 78 % of weight as rice and broken rice and bran, with the husk being the remaining 22% left. Rice mills use these husk to to generate steam for the parboiling process by burning them to generate heat for making steam in boilers. During such burning process as boiler fuel leads to formation of 25% ash (RHA) while the remaining 75% of the volatile matter is lost due to high temperatures to generate heat which is utilized. RHA has been found to contain around 85- 90 % amorphous silica. The moisture content has been reported to be around 8·68 - 10·44% with the bulk density ranging from 86 to 114 kg/ m^3. The percentage of silica in the rice husk usually varies from region to region. EDX studies have showed that the silica is mainly concentrated on the outer proturbances of the outer epidermis. In certain regions of India, RH is mainly used as cheap source of energy for parboiling paddy in rice mills. The product of combustion is partially burnt RH, which is completely a waste material and contributes to pollution. Utilization of this rice husk for production of silica solves these problems. All the different types of ash obtained by burning or pyrolysis of the rice husk produces ash, in general being called as Rice Husk Ash (RHA). The temperature of burning or pyrolysis varies the various forms of ash evolved. The time. temperature etc. of combustion effects the structural transformations of the silica sh. Amorphous silica is formed at around 550–800^{o}C and crystalline ash at greater temperatures. Sodium silicate when extracted from RH is hardly used directly. It can be

utilized after incorporation of transition metals on the silica to produce high potential heterogeneous catalyst via alkaline extraction routes.

Numerous techniques have been reported in the literature while all are following the basic technique of treatment with an alkali to solubilize the silica in form of alkali-silicate followed by precipitation with a concentrated mineral acid to obtain silica. Numerous cases of prior acid leaching/treatment of the rice husk before combustion or pyrolysis have been reported, where both mineral acids and organic acids have been reported to be used. Inorganic parts of the rice husk are removed by acid leaching and the breakdown of lignin and organic matter is accomplished, thus helping to obtain pure form of amorphous silica with lesser contaminants. Use of various acids for acid leaching like H_2SO_4, HCl, HNO_3, H_3PO_4, and also use of organic acids like oxalic acid, citric acid and acetic acid have been reported in literature. Precipitation of the sodium silicate has also been tried with various acids like HCL, H_2SO_4, H_2CO_3 etc. In the present work silica prepared from RH with and without acid leaching has been identified to be able to be used for impregnation with transition metal, presently with bi-metals, to produce evenly dispersed metals on the silica framework. Use of silica as catalyst support was popularized due to its high surface area available and its quality of having a narrow pore size distribution. The morphologies and properties of silica obtained from RH pyrolysed at various temperatures are also compared with each other. The structural changes and agglomeration of the silica obtained from RH pyrolysed at different temperatures are also observed.

1.3. Rice Husk Silica as Catalyst

Silica has been found to exist in form of gel, crystal and also in amorphous forms. SiO_2 structure is found to be based on the SiO_4 tetrahedral. Each Silicon atom is bonded to four oxygen atoms with each oxygen atom in turn getting attached to two silicon atoms. The silica surface consists of two types of functional groups, namely silanol (Si-O-H) and siloxane (Si-O-Si), with silanol being the more reactive one and with more adsorptive properties. Commercial silica is manufactured in a process involving multiple steps which involves high temperatures and pressure. This makes such a process less cost effective and not very environmentally friendly. Mobil Oil Company developed the

mesoporous material and it led to a huge research on such material and various metals incorporated on them. The inertness of silica and its ability to be custom tailored led to publication of around 3000 papers on mesoporous materials. The most common method for extraction of silica is solvent extraction. It is achieved either directly from the husk or the ash produced after pyrolysis of the husk. Better results are obtained on extraction of silica from the RHA instead of RH. Combustion at temperatures ranging from 550-800^{o}C leads to formation of silica on which metal can be impregnated, with higher temperature resulting formation of crystalline silica and reducing the available surface area.

Various types of synthesis procedures for preparation of mesoporous silica from rice husk and metals incorporation, have ben reported by several researchers. Aluminum sulfate, aqueous ammonia and nickel nitrate have been used by Tsay and Chang [12] to prepare Ni/RHA–Al_2O_3 via simple impregnation and ion exchange methods. Chen et. al. [13] have reported the preparation of copper impregnated RHA using the deposition–precipitation method followed by calcination at 673 K. Copper nitrate trihydrate has been used by Chang et. al. [14] as the copper source to produce copper impregnated silica. He achieved this via an incipient wetness impregnation method. Mesoporous molecular sieve (M41S) materials have also been extensively studied in details. Grisdanurak et. al. [15] have used CTAB as structure-directing agent (SDA) and synthesized MCM-41 mesoporous materials. Chlorinated volatile organic compounds were adsorbed and photocatalytic degradation of herbicide undergone using such materials developed. Manufacturing silica structural materials with desired pore size is influenced by varying parameters like silica source, type and concentration of surfactant, pH and the temperature of obtaining the silica precursor.

A lot of research is being carried out presently to produce environment friendly catalysts. Development of heterogeneous catalyst is advancing at a great pace which is evident from the huge number of research papers being available online in various journals. As we know, over the years, silica powders and gels have been widely used in industry as fillers, adsorbents, chromatographic agents, catalyst and as catalytic supports. Selection of a specific mechanism and a raw material for production of a catalyst is judged by its reusability and the ease with which it can be prepared. The effects of leaching on the catalyst is also an important criterion for catalyst selection. Use of

industrial waste, specifically rice husk, to prepare catalyst by sol-gel technique has been studied by Adam et.al. [16]. They reported the benzylation reaction of toluene with benzyl chloride. Insipient wetness method has also been used to develop metal supported catalysts from rice husk which has been reported by Chang et. al. [17]. High surface are asolids in particulate form can be developed by metal and metal oxide impregnation techniques on silica matrixes. Such composite oxides formed, differ from the binary oxides which are currently used as catalyst supports. The composite oxide are well dispersed on the support matrix and thus helps to obtain better catalytic results. Characterization of rice husk ash-supported nickel catalysts prepared by an ion exchange method has been reported by Tesh et. al. [18] to understand the interrelationship between the physical and chemical properties. Amorphous silica, extracted from rice husk by acid leaching, pyrolysis and carbon removal has been used as catalyst supports, owing to their high porosity and high surface area and has also been found to be impregnated with nickel metal, using ion exchange mechanism and used as an oxidation catalyst.

CHAPTER 2

LITERATURE REVIEW

2.1 Literature Review – General Outline

Silica, though having a simple formula of SiO_2, exists in a variety of forms in nature, leave aside synthetic forms. Each form of silica exhibits different physical and also chemical properties, existing in the form of gels, crystalline and amorphous forms. It is also at times fount to exist with other elements in form of ores or minerals. Silica is found in abundant quantities on earth, still for most technological applications silica is prepared by synthetic methods. Synthetic silica possess huge surface are which allows it to be used as adsorbing material and as catalyst support. In general the SiO_2 structure is based upon a SiO_4 tetrahedron. Each silicon atom is bonded to four oxygen atoms and again each oxygen atom being bound to two silicon atoms. Two types of functional group: silanol groups (Si-O-H) and siloxane groups (Si-O-Si) are present on the silica surface. All the chemical processes and even the physical processes like adsorption takes place on the silanol sites, the siloxane sites on the surface being inert to most of the activities. Generally the SiO_2 is a part of the SiO_2 tetrahedron structure, where each Si atom is bonded to four oxygen atoms and each oxygen atom in turn bonded to two silicon atoms [19]. Silica has also been reported to be found in some dicotyledonous plankton their husks or seeds like rice husk and foxtail millet. Porous amorphous silica has been found to contains isolated, germinal and vicinal as the three types of silanol bonds on its surface [20]. Isolated silanols have been found to be the more reactive species among all the three types found. An increase of temperature makes the silica surface more hydrophobic. The surface hydroxyl groups condense and form siloxane bridges. Commercial silica manufacture involves high temperature and pressure which renders it as a less cost efficient and non-environmental compatible process [21]. Considerable attention has been laid in recent years to modify catalytic surfaces, making it more efficient for reactions. Alternatives to conventional heterogeneous catalyst are possible by such chemical modifications of the silica obtained from RH. Amorphous silica which is usually produced commercially is a high energy consuming process, thus leading researchers to look for alternatives. Biogenic silica from rice husk has been extensively studied and various techniques applied on it to modify it with transition metals, metals and organic substances to catalyze various reactions. Heterogeneous catalysts have been prepared by immobilization of transition metal complexes and their nature and

mechanism has been studied and developed. This has also helped to manipulate the metal particle size and the crystalinity helping to achieve various catalytic reactions [22]. Side chain oxidation of styrene to produce benzaldehyde and styrene oxide is of considerable industry importance. Benzaldehyde is widely used as a starting material for various compounds in the pharmaceutical, dyes, resins, additives, flavours and organic solvents. Tungsten modified rice husk silica has been found to give 100% conversion of styrene with very less byproducts [23]. Heterogeneous catalysts along with greener oxidant like H_2O_2 and molecular oxygen have been reported to overcome some limitations of other heterogeneous catalysts and have drawn some serious research implications [24].Mobil Oil company developed mesoporous materials in the early 90's. Since then an extensive research was initiated in the silica field. Presently there are more than 3000 publications specifically in the area of mesoporous silica. Silica being chemically inert and the ease with which it can be structurally modified with metals and organic substances helped it to be widely considered as a catalyst support [11]. A vast amount of literature is available on amorphous silica, transition metal modified silica, heterogeneous catalyst on silica and rice husk derived silica which are briefly mentioned below.

2.2. Amorphous Silica Derived from Rice Husk Ash

Rice husk ash contains 85-95% silica and the rest of other inorganic materials. Research on extraction of this silica has been extensively documented over time. Alyosef et. al. [25] in have characterized biogenic silica generated by thermo chemical treatment of rice husk obtained from Egypt . they had optimized the process for least environmental impact by two routes vis. one by citric acid leaching the husk prior to pyrolysis and second without using acid leaching. Chandrasekhar et. al. [7] have treated rice husk with acetic and oxalic acid and used controlled burning techniques to prepare reactive white silica of high purity and also compared the results with rice husk treated with conventional mineral acids. Della et. al. [8] have also reported preparation and characterization of active silica with high surface area from rice husk ash. XRF, XRD, and particle size analysis had been conducted to characterize the silica formed. Similar work was also performed by P. Deshmukh et. al.[26] where they determined the silica activity index of the silica derived from rice husk ash under controlled heating conditions.

They had also performed XRD, and XRF studies. Kalapathy et. al. [9] had also derived silica from rice husk by simple alkaline extraction techniques but in form of xerogels which were later turned to aerogels. They characterized the materials using EDX, ICP (Inductively Coupled Plasma), and FTIR studies.

Several silica embedded materials and composites have also been developed and reported in literature. Rattanasak et. al. [27] have studied the development of high volume rice husk ash (RHA) alumino silicate composites (ASC) and later added with boric acid to prepare stable ASCs with compressive strengths up to 20MPa. Nayak and Bera [28] have developed a procedure for obtaining and characterizing active humidity indicating blue silica gel from rice husk ash after following the conventional technique of alkaline treatment and acid precipitation with impregnation with $CoCl_2$. The effect of calcination temperature and heating rate on the reactivity, surface area and optical properties of silica from rice husk has been studied by Chandrasekhar et.al. [29].

Production of amorphous silica from rice husk in fluidized bed system has been reported by Taib [30]. He designed and developed a pilot scale fluidized bed combustion system for the production of amorphous silica from rice husk. A review on processing, properties and applications of reactive silica from rice husk covering controlled burning techniques, production of reactive silica, pore structure and surface area studies and also various advanced material production like SiC, Si_3N_4 and Mg_2Si were summarized by Chandrasekhar et. al. [10].

2.3. Nano-Structured Silica from Rice Husk

Synthesis of biogenic silica nanoparticles from rice husks (RHs) as the raw material via controlled pyrolysis and catalysis by potassium ions to convert amorphous silica to crystalline phase were investigated by Wang et. al. [31]. He was successful in separating out silica nanoparticles of 20-30 nm dia. which had potential to replace fumed silica for various applications. Sol gel method was used by Le et. al. [32] to synthesize silica nanoparticles from Vietnamese rice husk. They studied the effect of surfactant surface coverage, aging temperature and aging time to produce 3 nm sized amorphous nano-silica with highest surface area of 340 m^2/g. Similar sol-gel techniques were also used by Adam et. al. [33] to produce mesoporous silica nanoparticles with an average

diameter of 50.9 nm and high specific BET surface area of around 245 m^2g^{-1}. Cetyltrimethylammonium bromide (CTAB) has been used as the surfactant at room temperature by Adam and Iqbal [24] to develop catalysts. They had developed silica–tin catalytic materials using simple sol–gel method.

2.4. Heterogeneous Catalyst

Heterogeneous catalysis refers to the group of reactions where the catalyst and the substrate are in different phases. Heterogeneous catalysts are mostly solids and the reactants are basically gases or liquids. A system where the catalyst is solid and the reactant is gaseous is the normal consideration while mentioning heterogeneous catalyst. Heterogeneous catalysis were mostly developed by the petrochemicals and bulk-chemicals industries and were usually built to withstand high temperatures, a requirement of chemical industries at large. Thus solid catalysts and gaseous reactants was the order of the use of catalyst in reactions like cracking. The facility of easy separation of a heterogeneous catalyst from the reaction medium is the most important advantage. The catalyst can be easily separated and cleaned in gas-solid systems, and easily filtered in in liquid/solid systems.

Heterogeneous catalysts are extensively used nowadays in various organic reactions like production of bio-diesel, oxidation of phenol, acetone, benzene or higher molecular weight compounds like styrene. Hydrogenation of acetone with heterogeneous catalysts has been achived at temperatures in the range of 100–300^oC. Hydrogenation of ace-tone to isopropanol with raney nickel and various nickel catalysts has also been reported [34]. Superactive catalyst consisting of nickel nano catalysts supported on silica obtained from tetraethyl orthosilicate (TEOS) have been studied and proved to be useful particularly for oxidation of acetone to isopropanol. There is an expanding research in the area of mono-dispersed silica nanospheres with lead on two-dimensional (2D) and three-dimensional (3D) ordered superstructures [35]. The temperatures of burning or pyrolysis have been found to alter the structural characteristics of the silica obtained. Higher temperatures have been found to form more crystalinity affecting the surface structure and catalytic effect in turn [36]. Acetone hydrogenation reaction with efficient selectivity has been performed by Gandhia et. al. [37]. The catalyst used by them had showed good

conversion at temperatures ranging from 180 to 220^{o}C. Ni/Ru bimetallic catalysts have been reported to be excellent catalysts for various reactions. These were found not to form solid solution or complexes between Ni and Pd or Pt [38, 39]. E-stilbenes have been synthesized with the aid of silica-supported palladium complex [40]. Silica supported molybdenum catalyst have also been synthesized, characterized and applied in the oxidation of various sulfides and olefins to their corresponding sulfoxides/sulfones and epoxides [41].

2.5 Amorphous Silica from Rice Husk as Catalyst Support and Synthesis Methodologies

Rice is one of the major crop in India producing about 22 million tonnes of rice husk being produced annually as a by-product most of which goes to waste or burnt in open fields. About 600 million tonnes of rice are produced each year. Every 1000 kg of paddy milled yields about 220 kg (22%) of husk[42]. The various components of RH are 20% ash, 38% cellulose, 22% lignin, 18% pentose and 2% other organic components [43]. Rice husk contains high percentage of amorphous silica mostly on its outer epidermis. Silica extracted from RH had been shown to be a good catalyst support for the synthesis of fine chemicals where iron and 4-(methylamino) benzoic acid have been incorporated into the sodium silicate, obtained from rice husk by a simple cost effective solvent extraction method. The resulting complex had been washed as a catalyst in the benzylation of toluene [44]. Researchers have found out that a conversion of around 27% was possible using chromium modified silica on oxidation of cyclohexane to ketone and alcohol products [45]

Rice husk is pyrolysed at high temperatures to generate RHA after which silica is extracted via an alkaline extraction route. All forms of the ash produced from burning rice husk in general is termed as Rice Husk Ash (RHA).The temperature of burning or pyrolysis varies the various forms of ash evolved. The time. temperature etc. of combustion effects the structural transformations of the silica sh. Amorphous silica is formed at around 550–800^{o}C and crystalline ash at greater temperatures. Amorphous silica is formed at around 550–800^{o}C and crystalline ash at greater temperatures. Sodium silicate when extracted from RH is hardly used directly. It can be utilized after

incorporation of transition metals on the silica to produce high potential heterogeneous catalyst via alkaline extraction routes. Various industrial reactions like oxidation of cyclohexane, cyclohexene and cyclohexanol, oxidation of phenylmethanol and decomposition of cyclohexanol has been performed with catalysts having silica as catalyst support [46]. The high surface area of the catalysts obtained gives it the high catalytic activity and conversion percentage.

Various types of synthesis procedures for preparing mesoporous silica incorporating metals and transition metals and also organic compounds from rice husk silica has been reported. Aluminum sulfate, nickel nitrate and aqueous ammonia had been used by Tsay and Chang [12] to prepare nickel modified RHA-Al_2O_3 catalyst using impregnation and ion exchange methods. Calcination at 673K has been used by Chen et. al. [39] to prepare Cu/RHA using the deposition–precipitation method. Methanol was oxidized partially to generate hydrogen using the above mentioned catalysts. Also Chang et. al. [14] described the synthesis of copper in RHA, using it for dehydrogenation of ethanol using copper nitrate trihydrate via an incipient wetness route. Mesoporous molecular sieve (M41S) materials have also been extensively studied in details. Grisdanurak et. al. [15] have used CTAB as structure-directing agent (SDA) and synthesized MCM-41 mesoporous materials. Chlorinated volatile organic compounds were adsorbed and photocatalytic degradation of herbicide undergone using such materials developed. Manufacturing silica structural materials with desired pore size is influenced by varying parameters like silica source, type and concentration of surfactant, pH and the temperature of obtaining the silica precursor.

The general procedure for extraction of silica followed is an alkaline extraction route followed by gel formation by addition of mineral acid. Later this gel is aged, centrifuged or filtered and finally dried. Addition of structural directing agent (SDA) to the gel during the extraction process helps to regulate the size of the ultimate particles. This SDA can later be removed from the dried powdered metal modified silica by calcination up to temperatures in which the SDA decomposes. Rice Husk Ash (RHA) is obtained by pyrolysis of the rice husk at the temperatures range of 500^oC to 800^oC for 5-6 hours in muffle furnace. These procedures have been modified according to the needs of the catalyst required. A black crude product had been developed by Chang et. al. [10]

pyrolyzed RH at 900^{o}C for 1 h in a furnace with N_2 flow. They also developed white ash by pyrolysis in atmospheric conditions. The effect of acid treatment, calcination temperature and the rate of heating of RH were studied by Chandrasekhar et. al. [47] reporting the effect on surface area.

Styrene was oxidized in its liquid phase with the help of tungsten modified silica as catalyst, as reported by Adam and Iqbal [23], using H_2O_2 as green oxidant for production of benzaldehyde. It was also reported that the pH of the preparation media had a strong influence on catalytic activity of the structure of the resulting silica-tungsten species. Zhang et. al. [48] reported that Mn–MCM-41 decomposes H_2O_2 very rapidly leading to very low styrene conversion. Other materials such as Cr–MCM-41, Fe–MCM-41, Mo–MCM-41 and V–MCM-41 had also been studied by them. Chromium incorporated rice husk silica synthesized at different pH was reported by Adam and Iqbal [24], where oxidation of styrene using hydrogen peroxide as the oxidant was studied. Chromium supported on mesoporous silica have been reported to also greatly steer the transformation of cyclohexane to cyclohexanone and cyclohexanol, which is required for the production of nylon-6 and nylon-66. Yao et al. reported a conversion of cyclohexane ca. 95% over Ce-MCM-41 at 100^{o}C over 12 hr giving 82% selectivity to cyclohexanol [49]. Silica-chromium catalyst incorporating 4-(methylamino)benzoic acid (MBA) into the RH silica framework has been reported to give 100% conversion of cyclohexane in a much shorter time, by Adam et. al. [46]. Adam and Fook [50] have also reported incorporation of Chromium into Rice husk without prior conversion of the husk to ash. They have used this to produce cyclohexanone and cyclohexanol from cyclohexane.

There is also number of publications based on silica from rice husk with metal incorporations by incipient wetness methods, but almost everywhere it has been found out that the catalyst is prone to metal leaching due to reaction. Among the preparation routes, incipient wetness impregnation is the one most frequently adopted in industry due to its simplicity and convenience but its utility is still limited by poor metal dispersion. To enhance metal dispersion, an inert material termed as ‘‘textural promoter’’ when introduced during preparation to separate the metal particles from contact with one another minimize the coalescence of metal particles. Such a textural promoter gives a relatively high melting point and helps to have somewhat smaller particles than those of

the active metal species. Owing to its high melting point (2708 K) and fine particle size, chromia (Cr_2O_3) was found to be a good textural promoter [51]. Chromia-promoted copper catalysts supported on RHA and on commercial silica gel have been prepared for comparison, to investigate the effects of chromia content on both the surface properties and the catalytic activity in ethanol dehydrogenation [52]. Template assisted sol-gel precipitation method has been used by Adam and Thankappan [53] to generate high surface area Cu-Ce incorporated rice husk silica catalysts. These were used for one-step oxidation of benzene using H_2O_2 as the oxidant in acetonitrile. They investigated the presence of Ce and Cu together in the silica matrix and the mechanism in which they enhanced catalytic activity.

Aluminium ions have been chemical incorporated into rice husk ash silica matrix by the sol-gel technique and the fatty acid adsorption capability have also been studied [54]. Actephenone has been oxidized using H_2O_2 in aqueous phase under mild conditions using vanadium incorporated RH silica leading to a cost-effective and green preparation route and has been reported by Adam et. al. [55]. Characterization of rice husk ash-supported nickel catalysts prepared by an ion exchange method has been reported by Tesh et. al. [18] to understand the interrelationship between the physical and chemical properties. It has also been reported that catalysts prepared by deposition-precipitation is stronger than that in the catalysts prepared by impregnation. Cluster compounds of metal oxides prepared by impregnation of supporting oxides with a precursor compound has been found to modify dramatically the interfacial properties of the bulk oxide and is referred to as composite oxides.

2.6. Transition Metal based Catalyst from Rice Husk

The reporting of sol-gel method to prepare transition metal impregnated amorphous silica heterogeneous catalyst by Adam and Cheah [56] led to the beginning of incorporation of chromium into the silica matrix. Oxidize cyclohexane, cyclohexene and cyclohexanol were achieved using the catalytic potential of the chromium-loaded catalysts. Cyclohexane conversion upto 27.13% were achieved on use of chromium–silica catalyst and a conversion of 12.69% on use of calcined chromium–silica catalyst.[46]. The effect of pH on the oxidation state of chromium and its influence in the

oxidation of styrene was also studied to identify which chromium species was more active in the oxidation reaction [24] with the catalysts being prepared at pH 10, pH 7 and pH 3.

Copper impregnated catalysts have also been prepared by sol-gel methods with and without calcination as a final step for catalyst preparation. Silica was extracted for this case from *foxtail millet* and oxidation of some tertiary amines using molecular oxygen as the oxidant and foxtail millet husk extracted silica supported copper as the catalyst under ambient conditions of temperature and pressure has been reported by Sivasubramanian et. al. [57]. Copper based catalysts have been widely used for degradation of phenol but usually found to have a very low yield [58]. Mesoporous material MCM41 had also been developed and used for oxidation of cyclopentene via a green route [59]. A new generation of materials called Hexagonal Mesoporous Silica (HMS) had been developed by Yang et. al. [60]. They impregnated these materials with tungsten and used them for selective oxidation of cyclopentene using H_2O_2 as an oxidation agent.

Molybdenum has also been instilled on the silica matrix from rice husk by sol gel methods [61]Tungsten species have been reported to be inserted into the silica matrix using the same method and conditions as mentioned above i.e. using sol-gel techniques [23]. The structure of surface active sites of tungsten–silica catalysts prepared in an acidic medium is shown in *Fig. 2.1*.

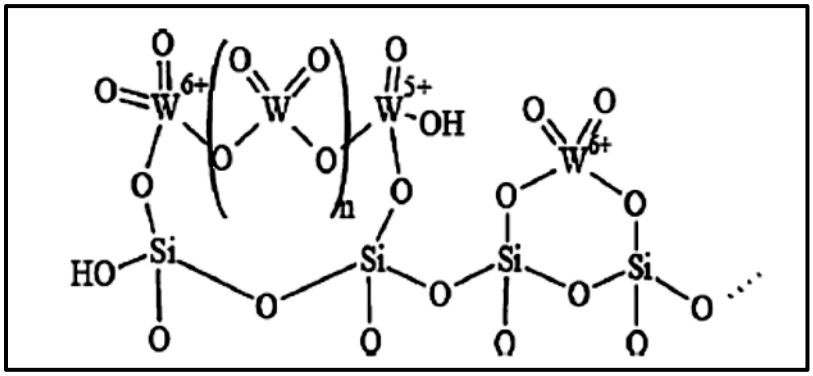

Fig 2.1: Tungsten–silica catalyst surface active sites (pH 3)

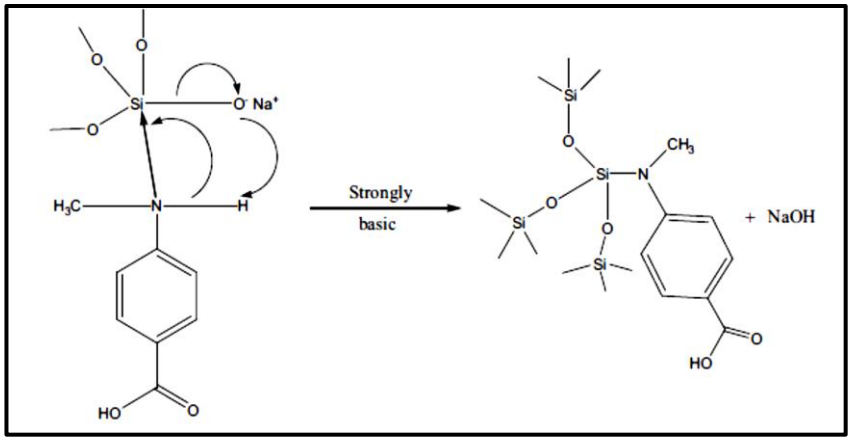

Fig 2.2: The Si-N bond formation of silica surface

Iron being a cheap transition metal has been also impregnated into the silica matrix and found to catalyze various reactions [44]. Iron had also been used for oxidation of phenol using hydrogen peroxide, after being instilled in the silica matrix [62]. Formation of the Si-N bond is shown in *Fig. 2.2*. Oxidation of phenol using hydrogen peroxide as oxidant has been reported in another study using a purely iron–silica catalyst [63]. Also an approach without the use of free radical mechanism was proposed by Umamaheswari et.al. [64] which prevented formation of benzoquinone, a usual product formed during phenol oxidation.

2.7. Silica Aerogels

Aerogels, which are highly porous, low-density materials consisting of nano-sized pores. The inertness and the mechanism with they can be structured according to the needs, make silica a usefull material for aerogel preparations too [65].Their applications are as varied as thermal insulation, catalysis, drug delivery, etc. [66].

The synthesis of silica aerogel can be divided into three general steps, which are (a) Preparation of gel, (b) Ageing of gel, and (c) Drying of gel. In the first step, colloidal system of liquid character changed into colloidal system of solid character in which the dispersed substance forms a continuous, coherent framework that is interpenetrated by liquid. The gel prepared is aged in its mother solution to strengthen the gel, so that shrinkage during the drying step will be a minimum. In the last step, the gel should be freed of the pore liquid. To prevent the collapse of the gel structure, drying is made to take place under special precaution [67].

The first attempt for the preparation of silica aerogel was by removing the liquid from a gel by a gas (air). The liquid held inside the gel has greater pressure than its vapour. To transform this liquid into a supercritical fluid (gas), a certain temperature is required which is known as critical temperature. Above that critical temperature the air can be replaced for that supercritical fluid to get a non-collapsed gel structure [68]. During drying under atmospheric conditions, the nanostructured porous layers are exposed to the capillary force and large surface tension, which destroys the microstructure and cause the shrinkage of the gel , as reported by Kistler [69]. Supercritical drying (SCD) method is usually used to solve this problem. In this process, the liquid in a substance is transformed into gas in the absence of surface tension and capillary stress. Thus, no

damage occurs to the material's delicate nanostructured pore network. However, the SCD is relatively an expensive process due to its high-pressure operating condition. For this reason there is a great interest in subcritical or ambient pressure drying. Ambient-pressure method for silica aerogel includes both surface modification and network strengthening of sol-gel derived silica wet gel. To prepare silica gel, silicon alkoxides like, tetramethoxysilane (TMOS), tetraethoxysilane (TEOS), methyltriethoxysilane (MTES) and polyethoxydisiloxane (PEDS) are mainly used [70-74]. In Ambient-pressure method, the water-alcohol mixture in the pores of the gel is first exchanged for a water-free solvent. Then, reaction with silylating agent takes place so that Si-OH groups are silylated. Silylation is carried out directly in the water phase of the hydrogel, which results in a solvent exchange as well as a phase separation of the gel water and the solvent. The replacement of H from the Si-OH groups by the hydrolytically stable Si-R groups through the oxygen bond prevents the adsorption of water and hence results in the hydrophobic aerogels.

All the silicon alkoxides materials are not only expensive but also hazardous and can cause blindness (with TMOS). Waterglass (or sodium silicate) solution was used for low-cost aerogel production by Kistler [69] using super critical drying method. Einarsrud et. al. [67] investigated properties of aerogels synthesized by different precursors and reported that waterglass, produced aerogel with the highest degree of monolithicity because these gels had the highest stiffness and the largest pore size. In the case of water

glass based aerogel, the sol preparation is quite different. The sol in this case is silicic acid (H_2SiO_3) which is produced by exchanging Na^+ ions of water glass with H^+. To remove sodium ions in the water glass, the dilute sodium silicate is passed through ion-exchange column filled with strong acidic cation resin such as sulphonated polystyrene. Adopting this ion exchanging technique, Lee et. al. [70] and Hwang et. al. [71] have prepared silica aerogel. But, Sarawade et. al. [72] had removed the sodium portion from the silica aerogel beads by washing with distilled water for 12 h. Silica aerogel was prepared in this study by ambient pressure drying method using sodium silicate as silica precursor. Li and Wang [75] prepared the aerogel through sol-gel process using both RHA and a small quantity of TEOS as modifier added into the hydro-sol.

Wang and Tang [73, 74] prepared silica aerogel from RHA by sol-gel process followed by supercritical drying. A new process for preparing silica aerogel was proposed. RHA, which is not only cheap but also rich in silica, was used as the silicon source. Li and Wang [6] prepared the aerogel through sol-gel process using RHA; a small quantity of TEOS was used as the modifier, and added into the hydro-sol. Then the aerogel was prepared by drying the gel at atmospheric pressure. Several authors have suggested that silica aerogel is a promising biocompatible scaffold for the immobilization of biological material for a variety of applications [76] and as matrices in the design of biosensors [77]. Fernandez et al [78] studied the preparation and bioactivity of wollastonite/aerogels composites obtained from a TEOS-MTES matrix through the sol-gel process. Bioactivity of this aerogel was studied by immersing it in SBF for 25 days. A spherical apatite layer covered the entire surface of the aerogel. Li et. al. [79] prepared protein encapsulated silica aerogel to form bio aerogel via the sol-gel polymerization of TEOS with an ionic liquid as the solvent and pore-forming agent and the solvent extraction process. The final gel was dried through Freeze-drying process. It was found that the DsRed protein was quite stable in this aerogel.

CHAPTER 3

EXPERIMENTAL PROCEDURES AND METHODOLOGIES.

3.1 Amorphous Silica from Rice Husk

3.1.1 Sample Preparation and Equipments Required

Rice husk (RH) was obtained from a local rice mill and initially the husk was washed thoroughly with water to wash off the mud and dirt in the husk. The samples after washing was drained of any water and dried in a drier at 90-100^{o}C overnight to obtain light weight rice husk. Considerable amount of such water washed RH was kept for the later procedures to be performed on. This water washed rice husk was termed as WWRH.

The equipment required are conical flask (150, 250, 500 ml), beaker (500, 1000 ml), pipette, burette, magnetic bead, magnetic stirrer with digital temperature control, measuring cylinder (50, 250 ml), petridish, Muffle furnace, drier, mortar pestle, ashless filter paper (Watmann 41 grade), normal filter paper (12.5 mm).

3.1.2 Acid Washing/Leaching

Water washed RH was added to 500 ml of 1N HCl for 1 hour in a beaker and heated upto a temperature of 90-100^{o}C. The solution after cooling was washed with plenty of water till the pH of the wash-out was near a range of 7. The RH was filtered out and dried overnight in a drier at 90-95^{o}C. The RH finally obtained was light weight and had a considerable amount of inorganic material removed due leaching. This Acid Washed Rice Husk was termed AWRH**.**

3.1.3 Preparation of Pyrolysed Rice Husk Chars

Pyrolysis of char was performed by using a Muffle furnace. Considerable amount of water washed rice husk was taken in a crucible and put in the furnace preheated to a temperature of 650^{o}C. The sample was kept in the furnace for 60 minutes and then removed and put inside a desiccator and left overnight. This procedure was followed for pyrolysis at various temperatures of 650, 750, 850^{o}C and termed as WWRH-A650, WWRH-A750, WWRH-A850.

Acid washed rice husk was also pyrolysed in the same procedure at temperatures ranging from 550, 650, 750^{o}C and termed as AWRH-A550, AWRH-A650, AWRH-A750 respectively.

3.1.4 Preparation of Amorphous Silica

A .Digestion

In a 250 ml conical flask of 150 ml of 2.5N NaOH was prepared and 4 gms of water washed rice husk ash- WWRH-A650 was added to it. The flask with its content was put on a heating plate maintained at a temperature of 85-95^{o}C with a magnetic stirrer and left for 90 mins. The solution turned transparent brown-black in colour with visible un-dissolved particles. This solution was cooled down and vacuum filtered using a grade 12 filter paper. The clear colourless filtrate contains the sodium silicate solution or water glass which was further used to obtain silica. Similar process was followed for rice husk ash (WWRH-A) obtained at other temperatures and also for AWRH-A obtained at different temperatures.

B .Precipitation

The clear sodium silicate solution was titrated with concentrated i.e. 35.4% HCl with constant stirring. On addition of HCl dropwise, white gelatinous precipitate starts to form which on stirring dissolves off. Further addition of acid results to more formation of precipitate and it continues till the pH of the solution has reached 7, after which no further precipitate is formed. This process is followed for sodium silicate solution obtained from all the rice husk ash i.e. WWRH-A and AWRH-A at various temperatures of pyrolysis.

C . Filtering and Finished Product

This precipitate obtained after precipitation is let to settle down and vacuum filtered using Whatmann 41 filter paper and later 50ml of boiling water is also added to the filter paper so as to wash off any NaCl formed due to the acid base side reaction. The residue left on the filter paper is pure white amorphous silica which is dried in an oven at 90^{o}C and later the silica scrapped off the dried filter paper and stored in sampling bottles for further analysis and characterization.

Similarly silica in pure form is also obtained from ash obtained from pyrolysis of acid leached rice husk. These silica, both obtained from acid washed and water washed RHA are kept separately in sampling bottles for later use in characterization and termed Rice Husk Silica (RhSi)

3.2. Metal Modified Silica Catalyst from Rice Husk

3.2.1 Acid Washing

Rice husk (RH) was obtained from a local rice mill and initially the husk was washed thoroughly with water to wash off the mud and dirt in the husk. The samples after washing were drained of any water and dried in a drier at 90-100^{o}C overnight to obtain light weight rice husk. Water washed RH was added to 500 ml of 1N HNO_3 for 1 hour in a beaker and heated upto a temperature of 90-100^{o}C. The solution after cooling was washed with plenty of water till the pH of the wash-out was near a range of 7. The RH was filtered out and dried overnight in a drier at 90-95^{o}C. The RH finally obtained was light weight and had a considerable amount of inorganic material removed due leaching. This Acid Washed Rice Husk was termed AWRH**.**

3.2.2. Controlled Pyrolysis to Produce Rice Husk Ash

Pyrolysis of char was performed by using a Tubular Furnace. Considerable amount of AWRH-N was taken in a crucible and put in the furnace programmed at a temperature rise of 5^{o}C/min upto 750^{o}C and held at that temperature for an hour. The sample after removal were kept in a desiccator overnight. These samples were termed as AWRHA-N.

3.2.3. Preparation of Metal Modified Silica from Rice Husk

A. Digestion

In order to prepare the metal modified silica catalyst 4 gms of AWRHA-N after controlled pyrolysis in the tubular furnace were added to 150 ml of 2.5N NaOH and also 50 ml of 0.01M CTAB solution was added to the alkali and heated on a magnetic stirrer for 90 mins at 85- 95^{o}C. The resulting transparent brown solution was filtered using Whatmann 41 filter paper to obtain clear sodium silicate solution containing CTAB as Structural Directing Agent (SDA). This sodium silicate will act as the silica precursor.

B. Precipitation

This sodium silicate was titrated with 3M HNO_3 solution containing dissolved 10% (w/w) Chromium in form of Chromium Nitrate and 5% Copper in form of

Copper Nitrate. Light Green precipitate starts to form on addition of the acid and continues further as the pH is reduced. Precipitation is led to continue upto three different pH of 10, 7 and 3. The pH is constantly checked constantly while the acid is added dropwise and also with constant stirring on a magnetic stirrer. On reaching the desired pH the acid with loaded metal ions is stopped. The gelatinous precipitate is removed from the vessel and left aside. This gel formed is the gel form of the metal modified silica. Similar procedure is also used to extract bi-metal modified silica with higher copper loading, i.e. titration is carried out with 3M HNO3 having 10%Cr and 10% Cu salts dissolved in the acid following the same procedure and again upto three different pH of 10, 7 and 3.

C. Drying and Product Finishing

The precipitate is led to age for 24 hrs and then centrifuged and separated out, dried overnight at 90^{o}C. The dried samples were ground to fine powder using mortar-pestle and calcined at 300^{o}C for 3 hrs to remove the CTAB in the silica and labeled RhSi-Cr/Cu-10, RhSi-Cr/Cu-7 and RhSi-Cr/Cu-3 respectively after a final grinding in mortar-pestle. The samples having 10%Cr and 10% Cu were also also separated after aging from the solution by centrifugation, dried and ground to powder form. They were also calcined at 300^{o}C to remove the CTAB in the silica and finally ground to obtain dark brow-green powdered catalyst.

3.3. Oxidation of Styrene in Liquid Phase.

Oxidation of styrene to benzaldehyde and styrene oxide and its conversion and selectivity studies were conducted using these metal modified silica catalysts RhSi-Cr/Cu-10, RhSi-Cr/Cu-7 and RhSi-Cr/Cu-3 having 10%Cr and 5%Cu loading and also for RhSi-Cr/Cu-10 having 10%Cr and 10%Cu loading.

A 50 ml round bottom flask was used to carry out the oxidation test. The reactants 10 mmol of styrene, 20 ml acetonitrile, and 100 mg of catalyst were added and mixed in the flask and heated to 353K in a paraffin oil bath. The round bottom flask was fitted with a reflux condenser on the top to avoid loss of volatiles from the reaction medium. Once the reaction has processes and the desired temperature attained, 40 mmol of dilute hydrogen peroxide (30%) was added to the flask and reaction let to further continue. The

catalyst powder was filtered out after 30 mins and the reaction let to continue with the filtrate for 6 hrs in total. 1 ml of aliquots of the solution were removed every hour and 5µl of m-xylene added to the aliquots before GC-MS analysis. The experimental setup for the liquid phase oxidation of styrene is shown in *Fig 3.1* below. The oil bath was kept on a heating plate and temperature controlled upto the desired level. The reflux condenser was removed hourly and 1ml of the reaction mixture pipetted out into sampling bottles. Thus we get six samples, each at every hour and GC analysis conducted on them.

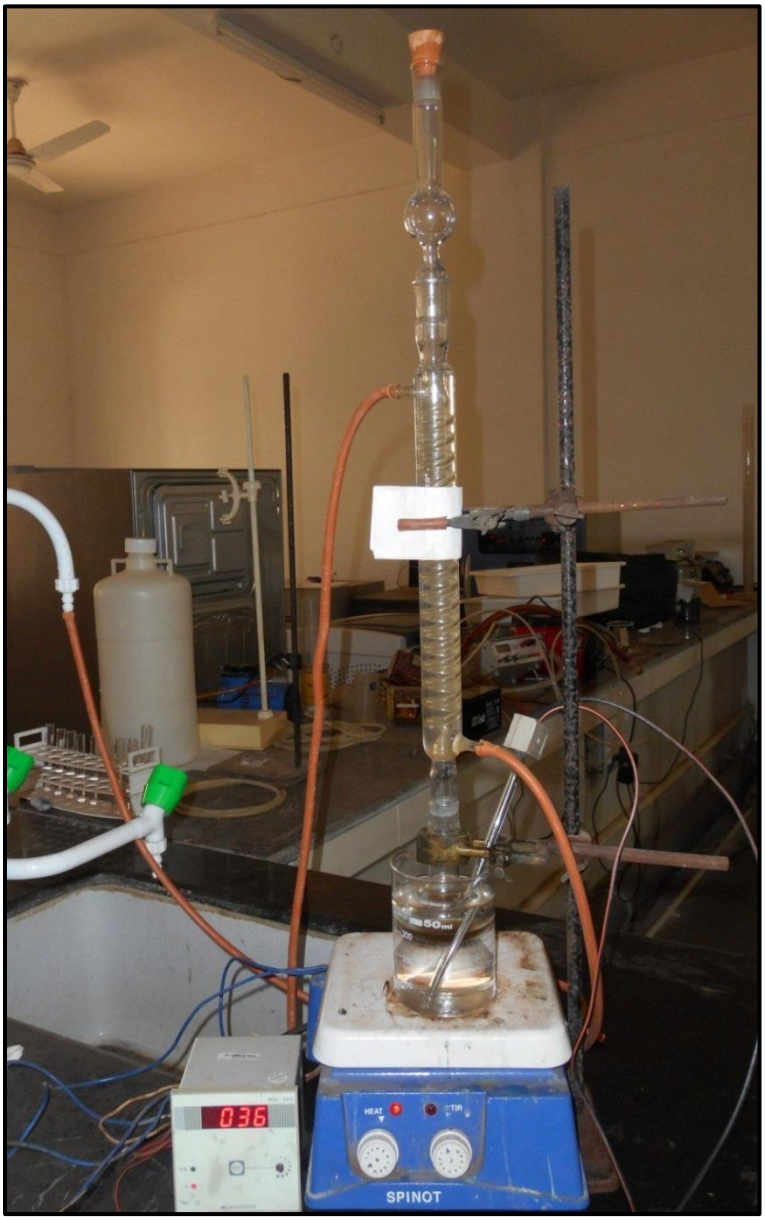

Fig 3.1: Experimental setup for liquid phase oxidation of styrene

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1Structural Features of RHA, Silica from RH and Metal Modified Silica Catalyst

4.1.1 XRD Analysis of Pyrolysed Char

The X-Ray diffraction intensity of the acid washed pyrolysed ash, AWRH-A650, AWRH-A750, and AWRH-A850 was performed using "Panalytical X'Pert^3 Powder" diffraction system. The X-Ray diffraction patter of the silica sample was recorded at a range of 10 – 80^o 2θ Bragg's angle.at a scanning speed 3 deg min^{-1}. The X-ray being produced from CuK_α radiation and after use of a Ni filter. The powder sample for the XRD was prepared on metal plate and pressed to have a flat surface. The XRD was carried out at a voltage of 40 kV and 30 mA current intensity. The XRD diffraction patterns of the three samples are shown in *Fig 4.1*, *Fig 4.2* and *Fig 4.3* below. No definite peaks were identified but a pattern list with a presence of silica, quartz and calcite was identified for samples pyrolysed at 750^{o}C, a peak at 26.72^o 2θ indicating presence of crystalline quartz which was formed due to increase in pyrolysis temperature.

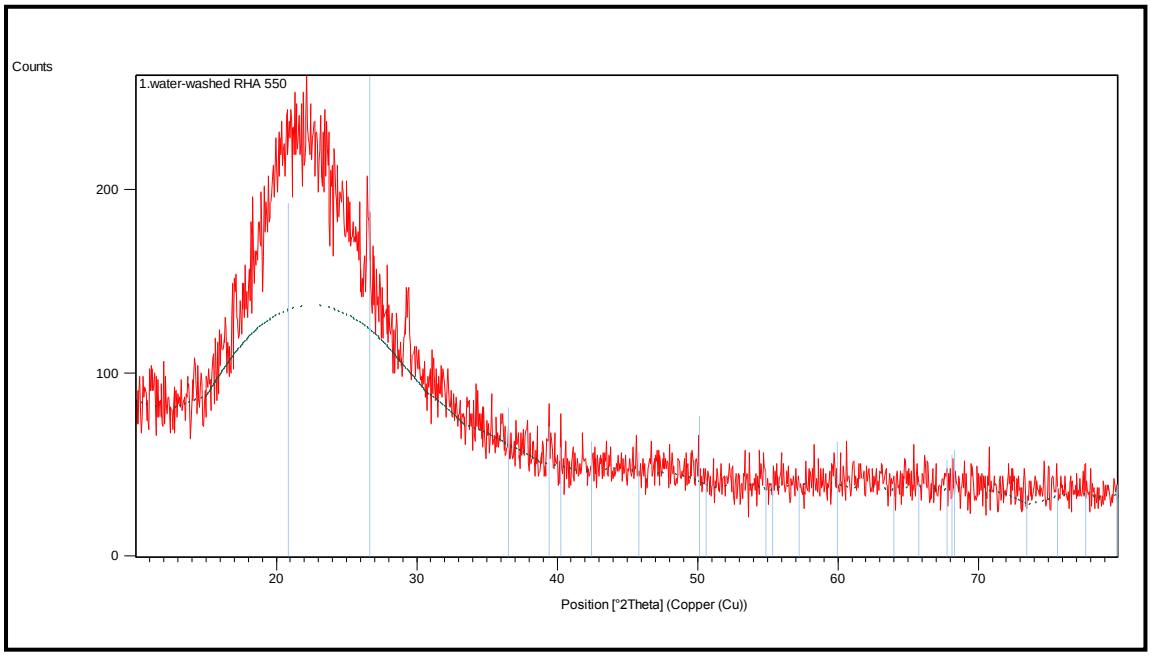

Fig 4.1: Main Graphics, Analyze View of RHA pyrolyzed at 650^{o}C showing a pattern

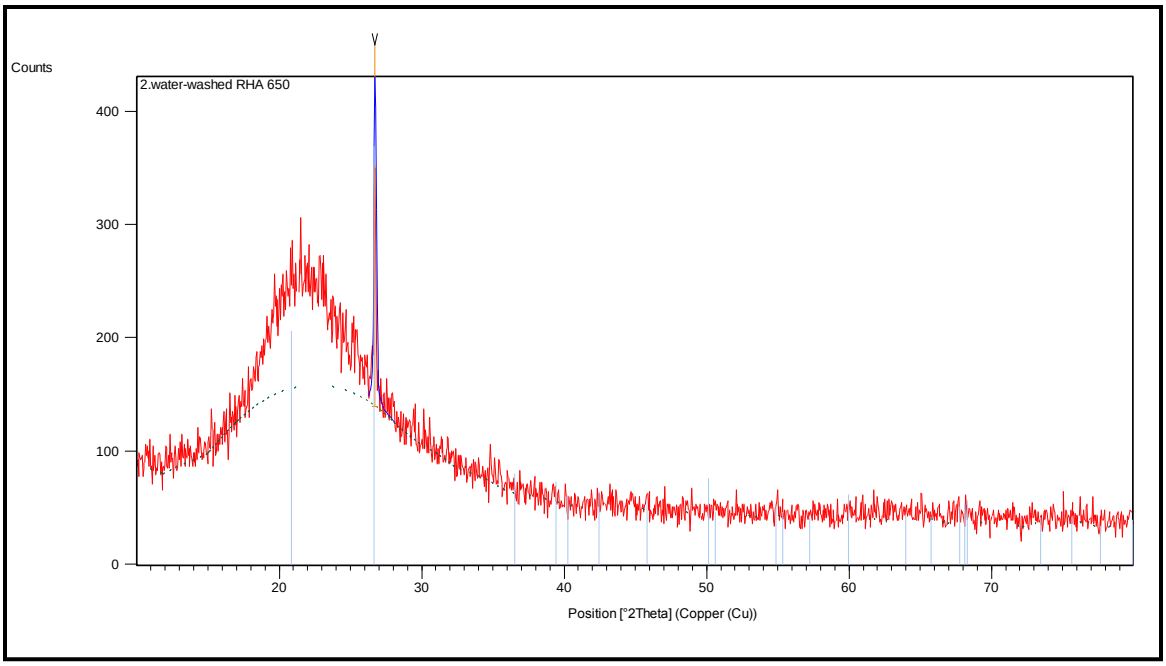

Fig 4.2: Main Graphics, Analyze View of RHA pyrolyzed at 750^{o}C showing a single peak

XRD scan of silica obtained from rice husk pyrolysis at 750^{o}C and 850^{o}C shows the presence of a single peak confirming presence of silica and quartz in the sample.

Table 4.1: *Peak List of RHA pyrolyzed at 750^{o}C*

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
26.5500	110.20	0.1800	3.35459	100.00

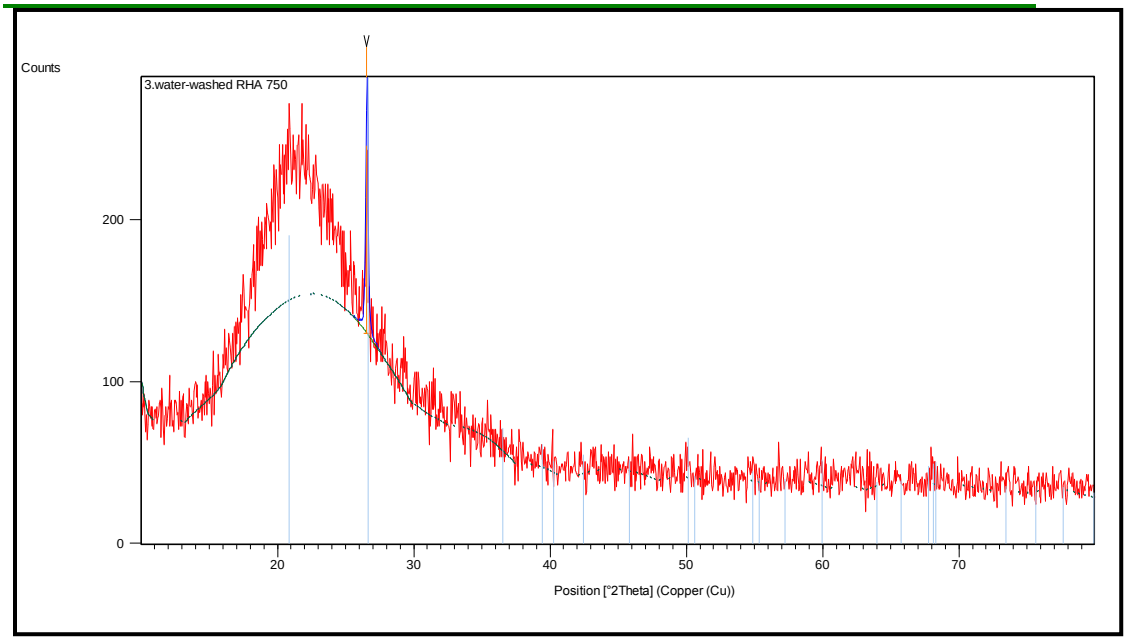

Fig 4.3: Main Graphics, Analyze View of RHA pyrolyzed at 850^{o}C showing a single peak

4.1.2. XRD Analysis of Silica Obtained from RHA

Silica obtained from the RHA by thermo chemical extraction techniques was also analyzed by X-ray diffraction technique. Silica obtained from acid washed rice husk after pyrolysis was used for this purpose. A scanning range of 10^{o} to $80^{o}2\theta$ was used with a step size of 3 was used. RHA obtained at temperatures of $650^{o}C$,$750^{o}C$ and $850^{o}C$ after acid washing were used. All the samples showed no presence of crystalline i.e. ordered crystalline structure other than Na and Cl obtained from the titration process. The diffraction patterns are shown below in the *Fig 4.4, 4.5* and *4.6.* A reference comparision with JCPDS data has shown presence of sodium and chlorine compounds. No peak at region of around $26^{o}2\theta$ confirms absence of crystalline quartz or crystoballite.

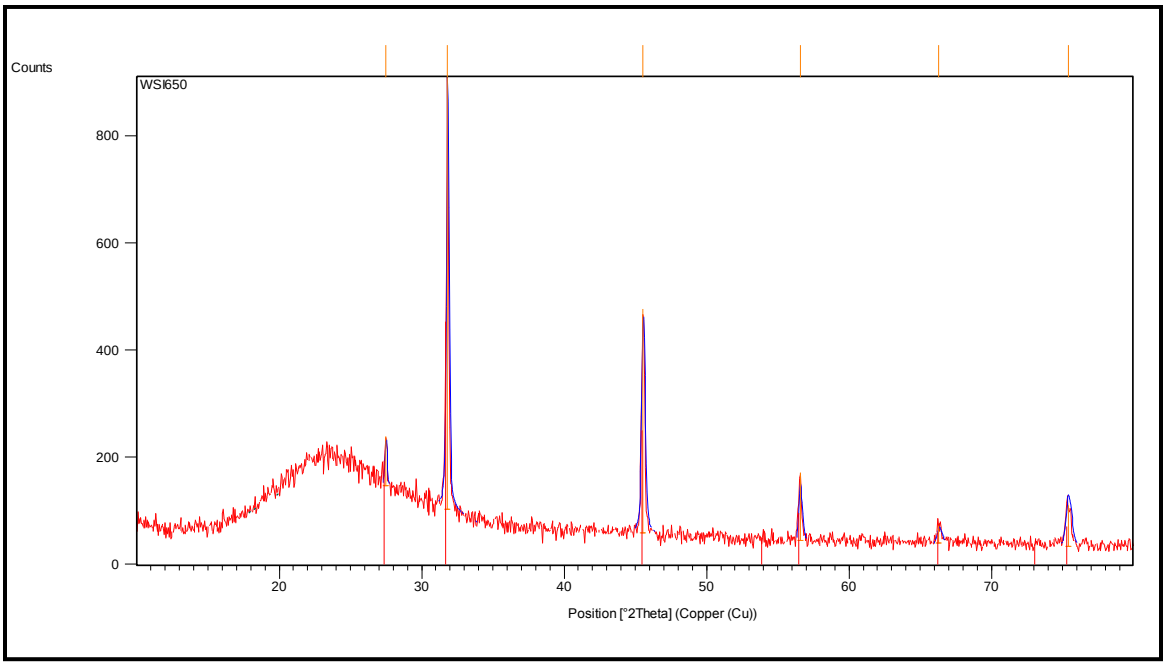

Fig 4.4: Main Graphics, Analyze View of silica from RHA pyrolyzed (acid washed) at $650^{o}C$

Table 4.2: *Peak List:(Silica from RH pyrolysed at $750^{o}C$)*

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
27.4280	145.65	0.1476	3.25187	9.96
31.7900	1462.81	0.1968	2.81492	100.00
45.5143	825.85	0.2460	1.99298	56.46
56.5219	202.89	0.2460	1.62821	13.87
66.2756	143.56	0.1476	1.41028	9.81
75.3009	162.78	0.2400	1.26104	11.13

Table 4.3: *Pattern List: (Silica from RH pyrolysed at 750^{o}C)*

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	00-005-0628	77	Halite, syn	0.000	0.490	Na Cl

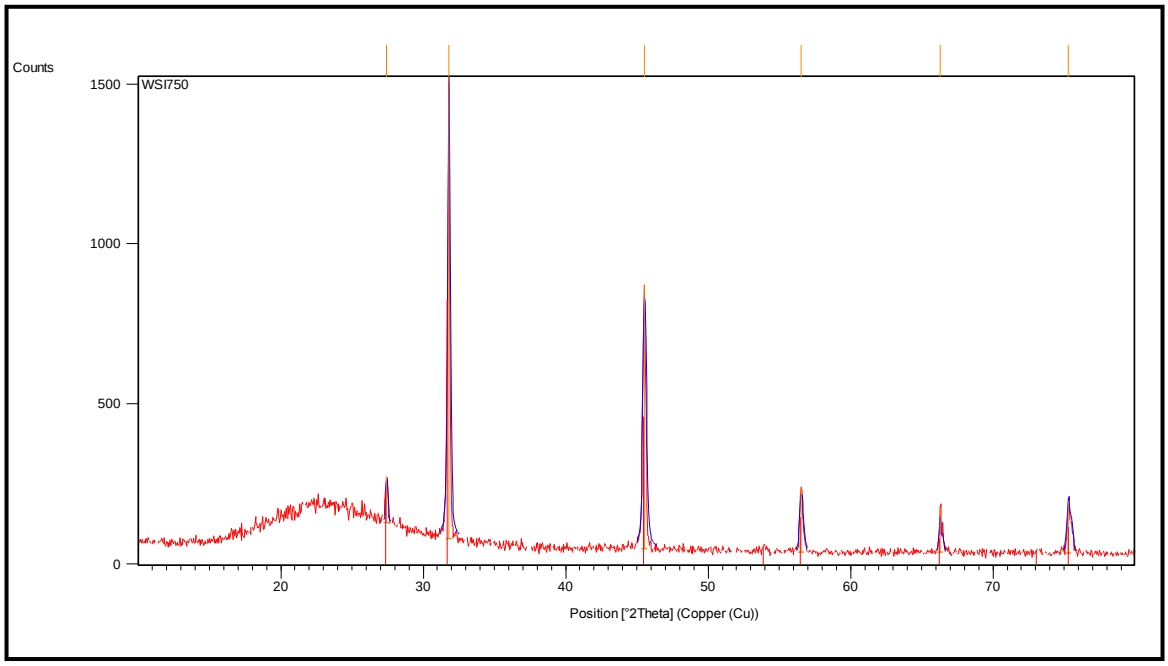

Fig 4.5: Main Graphics, Analyze View of silica from RHA pyrolyzed (acid washed) at 750^{o}C

Similar patterns are also seen for silica obtained by pyrolysis at 750^{o}C and 850^{o}C. Presence of Halide i.e. Na and Cl is also seen after analysis.

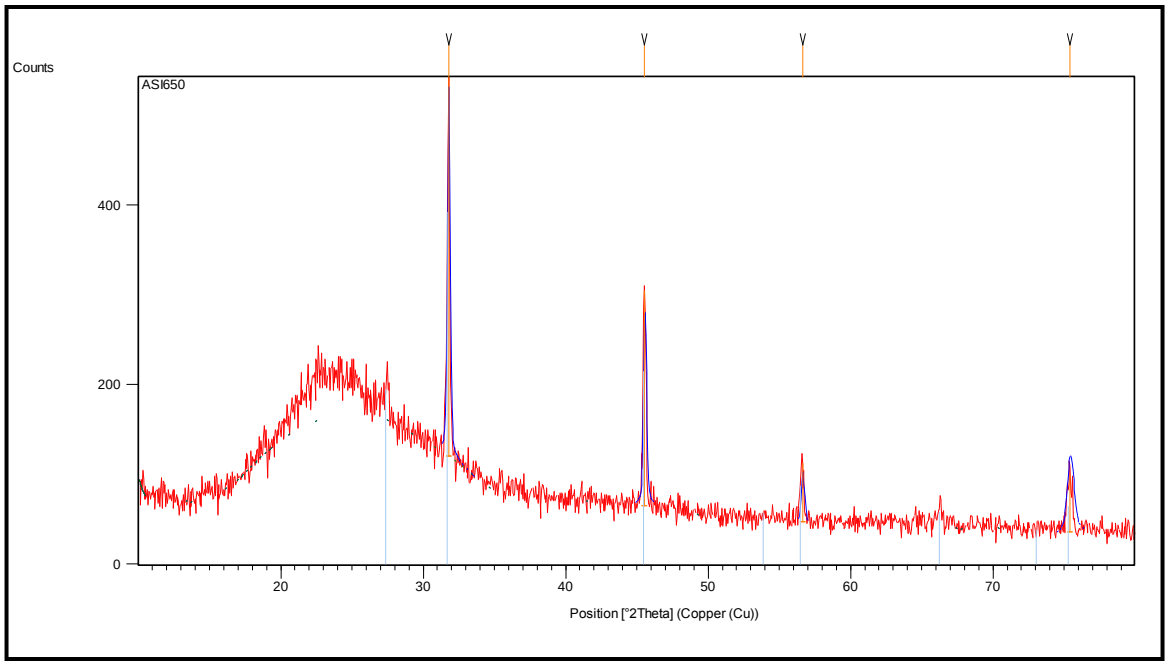

Fig 4.6: Main Graphics, Analyze View of silica from RHA pyrolyzed (acid washed) at 850^{o}C

4.1.3. XRD Analysis of Transition Metal Modified Silica Catalyst Obtained from RHA

Transition metal modified silica heterogeneous catalyst obtained from the RHA by thermo chemical extraction techniques was also analyzed by X-ray diffraction technique. Chromium and Copper modified amorphous silica catalyst prepared by sol-gel techniques were used. Both catalyst groups with 10%Cr –5% Cu and 10%Cr – 10%Cu were analyzed and presence of Chromium and Copper were confirmed. A scanning range of 10^{o} to 80^{o}2θ was used with a step size of 3 was used. RHA obtained by pyrolysis at temperatures of 750^{o}C under N_2 atmosphere after acid washing (dil. HNO_3) were used to obtain the silica. All the samples showed presence of crystalline i.e. ordered crystalline structure, and Chromium and copper conjugates with Silica along with presence of Copper Silicide.

Fig 4.7, 4.8 and *4.*9 show the XRD patterns of the metal modified silica with lower percentage of Copper loading, i.e. 5%Cu with the constant 10% Cr only extracted upto pH of 10, 7 and 3 respectively. The *Tables 4.4, 4.5, 4.6 and 4.7* show the

Peak List and Pattern List of Metal Modified Silica Catalyst obtained at pH of 10 for the samples with 10%Cr and 5% Cu loading.

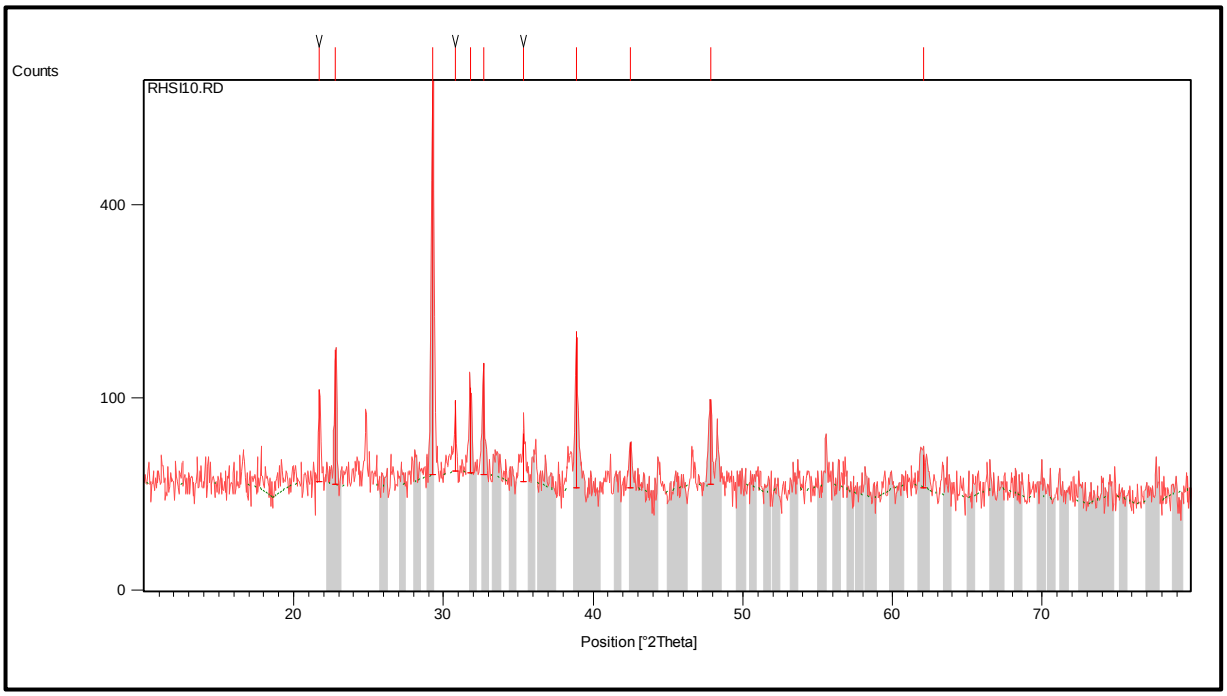

Fig 4.7: Main Graphics, Analyze View of Metal Modified Silica Catalyst with 10%Cr – 5%Cu from RHA extracted at pH of 10

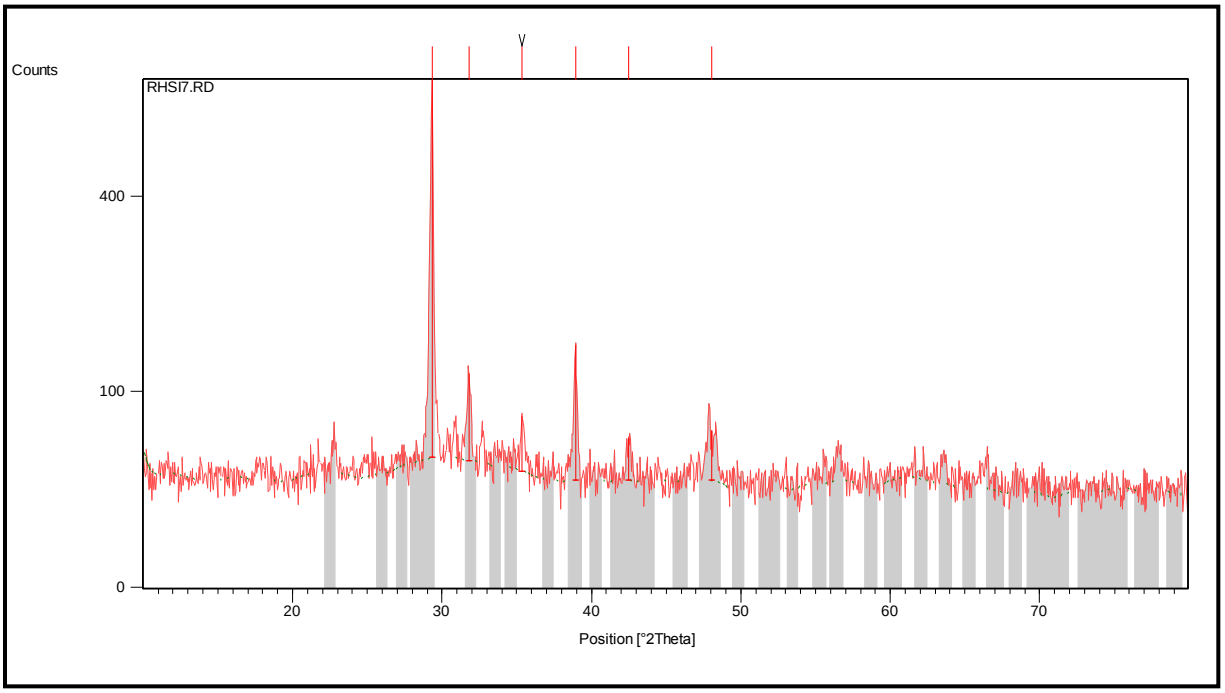

Fig 4.8: Main Graphics, Analyze View of Metal Modified Silica Catalyst with 10%Cr – 5%Cu from RHA extracted at pH of 7

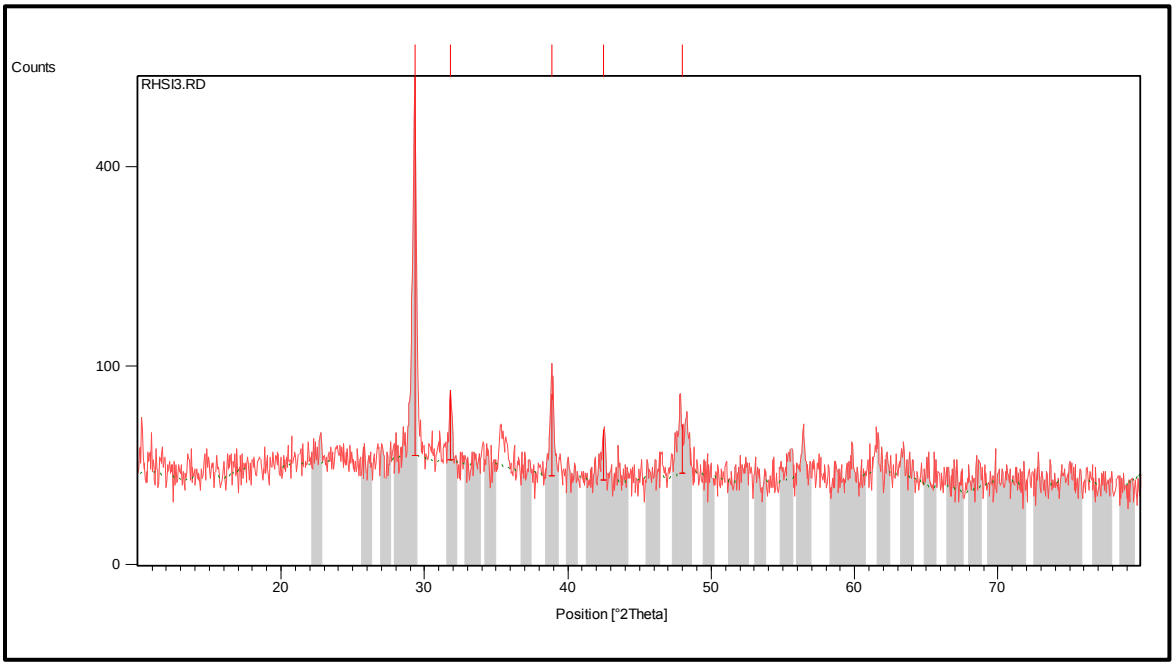

Fig 4.9: Main Graphics, Analyze View of Metal Modified Silica Catalyst with 10%Cr – 5%Cu from RHA extracted at pH of 3

Table 4.4: ***Peak List:*** 10%Cr – 5%Cu modified Silica extracted at pH of 10

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
21.7258	76.57	0.1476	4.09074	11.48
22.7940	126.38	0.1476	3.90139	18.95
29.2985	666.99	0.1476	3.04837	100.00
30.8006	59.72	0.1476	2.90305	8.95
31.8053	73.94	0.1476	2.81360	11.09
32.6749	103.10	0.1476	2.74068	15.46
35.3292	34.54	0.3936	2.54062	5.18
38.9019	152.60	0.1476	2.31513	22.88
42.5007	30.94	0.2952	2.12705	4.64
47.8267	68.28	0.1968	1.90188	10.24
62.0475	21.91	0.7200	1.49458	3.28

Table 4.5: ***Pattern List:*** 10%Cr – 5%Cu modified Silica extracted at pH of 10

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	76-1800	6	Copper Silicon	0.000	0.192	Cu15 Si4
*	23-0223	5	Copper Silicon	0.000	0.040	Cu0.83 Si0.17
*	39-0973	4	Silicon	0.000	0.032	Si
*	72-1326	3	Chromium Silicon	0.000	0.127	Cr Si

Fig 4.10, 4.11 and *4.12* show the XRD pattern of the group of metal modified rice husk silica catalyst having greater percentage of Copper loading. The samples have 10%Cr and 10%Cu too. The catalysts were extracted by sol-gel methods upto pH of 10, 7 and 3 respectively. The *Tables 4.8* and *4.9* show the Peak List and Pattern List of Metal Modified Silica Catalyst obtained at pH of 3 for the samples with 10%Cr and 10% Cu loading only.

Table 4.6: ***Peak List:*** 10%Cr – 10%Cu modified Silica extracted at pH of 10

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
22.8864	43.18	0.2952	3.88584	12.30
29.3342	350.94	0.1968	3.04475	100.00
31.7947	48.99	0.2952	2.81451	13.96
35.3935	28.55	0.5904	2.53615	8.13
38.9713	77.54	0.2952	2.31117	22.10
47.9109	32.48	0.7200	1.89716	9.25

Table 4.7: ***Pattern List:*** 10%Cr – 10%Cu modified Silica extracted at pH of 10

Vis	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	76-1800	10	Copper Silicon	0.000	0.250	Cu15 Si4
*	39-0973	6	Silicon	0.000	0.537	Si
*	01-1261	4	Chromium	0.000	0.036	Cr
*	75-0841	4	Silicon	0.000	0.438	Si
*	03-0990	3	Copper Silicide	0.000	0.300	Cu4 Si
*	72-1326	4	Chromium Silicon	0.000	0.578	Cr Si

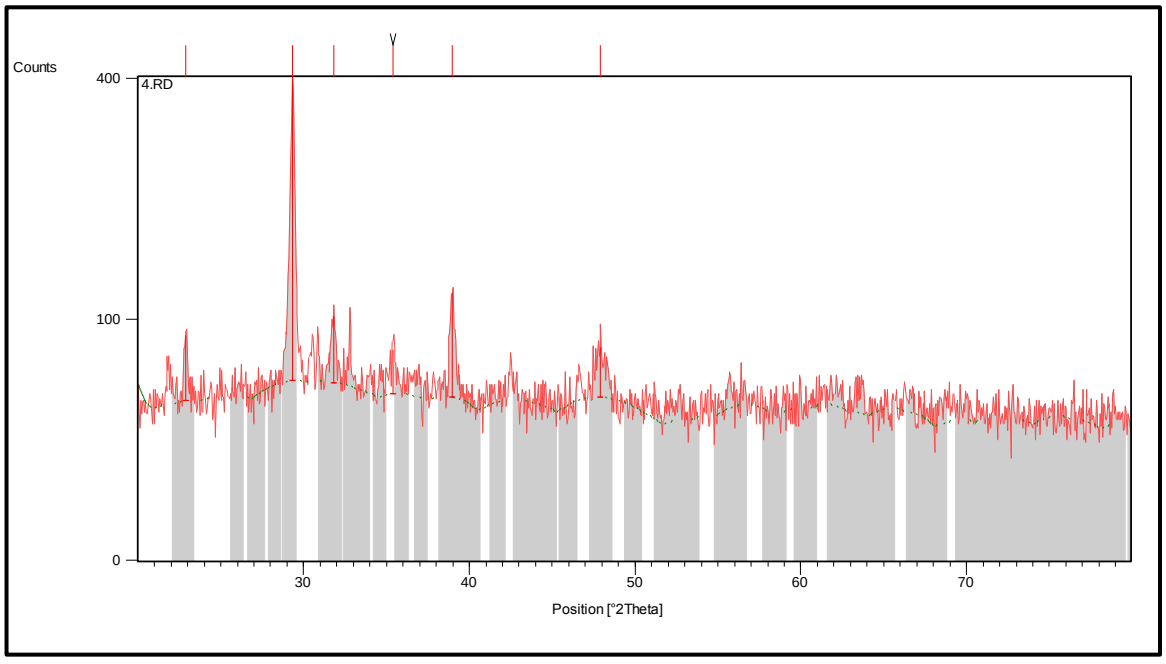

Fig 4.10: Main Graphics, Analyze View of Metal Modified Silica Catalyst with 10%Cr – 10%Cu from RHA extracted at pH of 10

A comparision with the XRD peak pattern of Silica obtained from RHA by alkaline extraction, wherein the RH is itself HNO_3 washed, with the XRD patterns of Cr-Cu modified silica from RH, with similar prior acid washing has shown a broad peak at $2\theta = 23^o$. The presence of this peaks suggests the presence of amorphous silica in the catalyst sample. The absence of other peaks in the silica without transition metal impregnation in RHSi 550, RHSi 750 and RHSi 850 indicate that the Cr_2O_3 and CuO crystals did not form on the silica surface. The XRD patterns of metal modified silica also depicts that the Chromium and Copper species are evenly spread out on the silica matrix. The broad peaks at round 23^o 2θ started to split and new peaks at 22, 29, 31, 38 and 47^o 2θ began to on impregnation of transition metal and and on reduction of the pH at which the metal modified silica catalysts were extracted. Peaks and pattern list of silica catalyst with higher metal loading extracted at pH of 3 is shown in *Tables 4.8* and *4.9*. Reduction of pH also led to more shift of the peaks toward the higher angle side, i.e. toward 45-47^o 2θ.Larger metal crystals are formed with pH reduction more amount of metal is being impregnated into the silica matrix which in turn causes phase segregation.

A comparision of the peaks for metal modified silica catalyst with lower amount on Copper loading, i.e. 10%Cr – 5%Cu, with the catalyst having higher amount of Copper loading, i.e. 10%Cr – 10%Cu, showed the split in peaks at 21, 30, 32, 42 and 62 converge at single peaks around them. This can be accounted for formation of complexes within Cr and Cu and their crystals on the silica surface, also higher amounts of Cu leaving a greater impression on the XRD patterns.

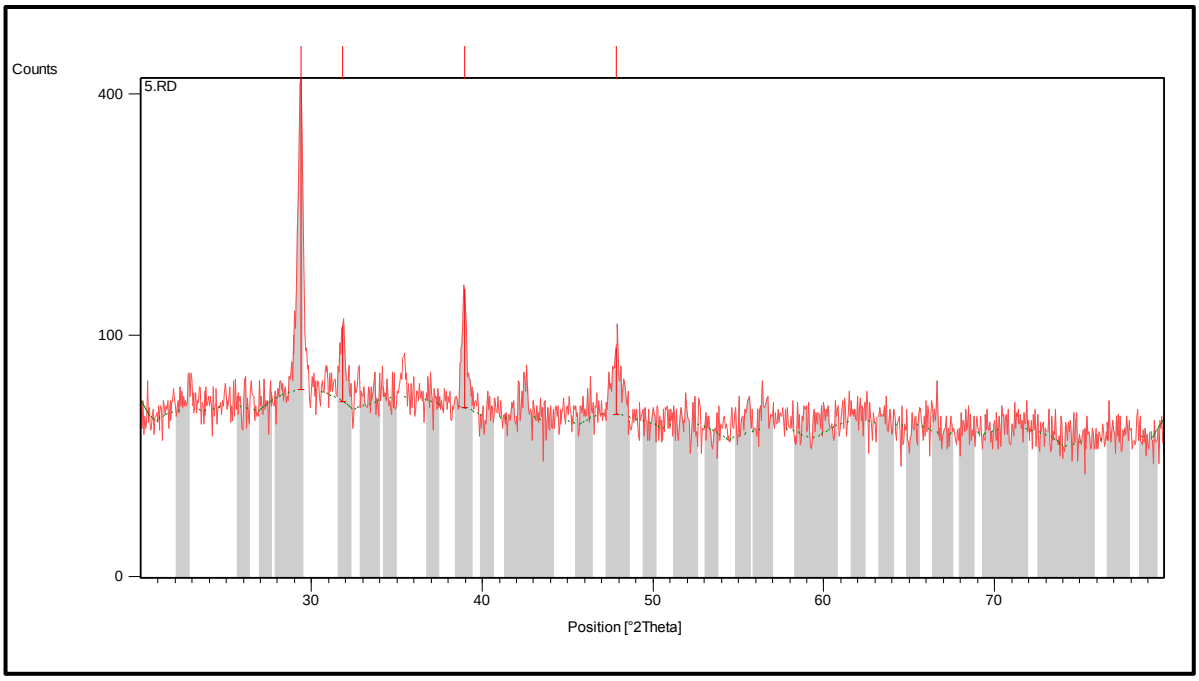

Fig 4.11: Main Graphics, Analyze View of Metal Modified Silica Catalyst with 10%Cr – 10%Cu from RHA extracted at pH of 7

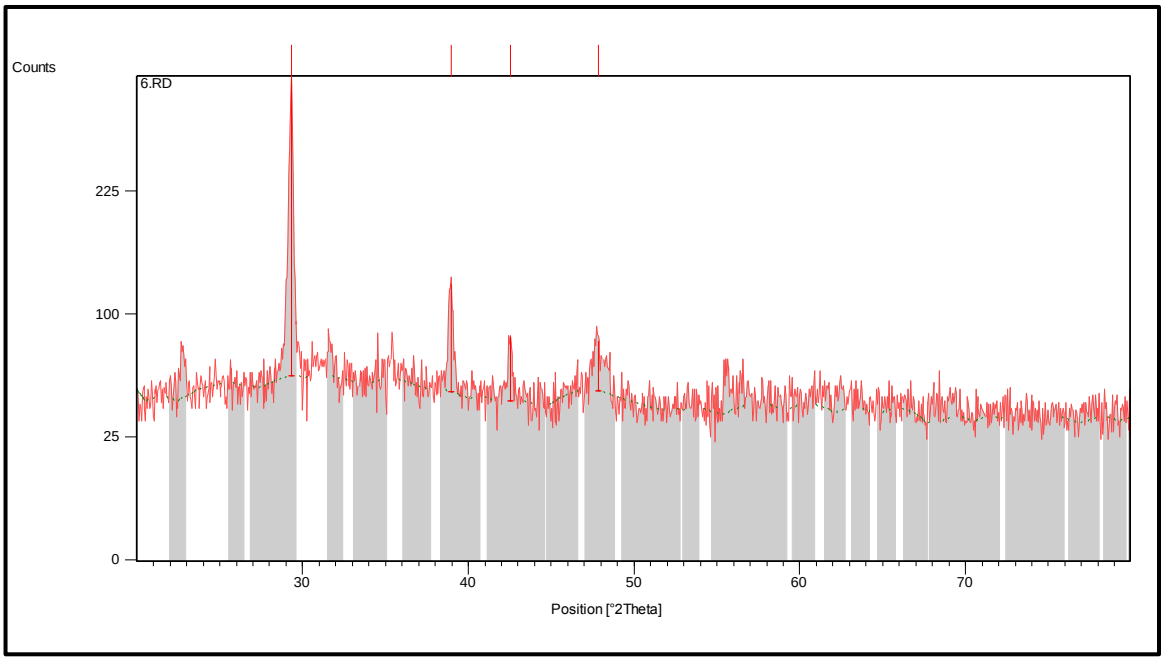

Fig 4.12: Main Graphics, Analyze View of Metal Modified Silica Catalyst with 10%Cr – 10%Cu from RHA extracted at pH of 3

Table 4.8: ***Peak List:*** 10%Cr – 10%Cu modified Silica extracted at pH of 3

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
29.3042	329.39	0.1968	3.04779	100.00
38.9415	79.07	0.2460	2.31286	24.01
42.5261	40.87	0.2952	2.12584	12.41
47.8491	32.28	1.2000	1.89947	9.80

Table 4.9: ***Pattern List:*** 10%Cr – 10%Cu modified Silica extracted at pH of 3

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	01-0791	15	Silicon	0.000	0.036	Si
*	23-0223	11	Copper Silicon	0.000	0.079	Cu0.83 Si0.17
*	47-1186	13	Silicon	0.000	0.722	Si
*	03-0990	6	Copper Silicide	0.000	0.369	Cu4 Si
*	76-1800	9	Copper Silicon	0.000	0.195	Cu15 Si4
*	72-1326	4	Chromium Silicon	0.000	0.370	Cr Si

4.2. FESEM Images and EDX Analysis of RHA, Silica from RH and Metal Modified Silica Catalyst

4.2.1. SEM and EDX of RHA (pyrolyzed)

Rice husk pyrolyzed, after acid wash and pyrolysed at 750^{o}C has been tested under FESEM and Energy Dispersive X-Ray technique was used to identify the components in the ash. The FESEM images of the ash showing the pyrolyzed condition of a single rice husk inner surface in 100X magnification, with a 500X magnification in the inset is shown in *Fig 4.13*. The EDX analysis confirmed the presence of silica and oxygen in the ash. Silica was found to be present in about 16.8% of the ash. The SEM image of the same ash but showing the outer shell of the husk with proturbances is shown in *Fig 4.14* and an EDX analysis shows 34% of silica on the outer part of the husk confirming that the amorphous silica in the husk lies mainly on the outer epidermis of the husk.

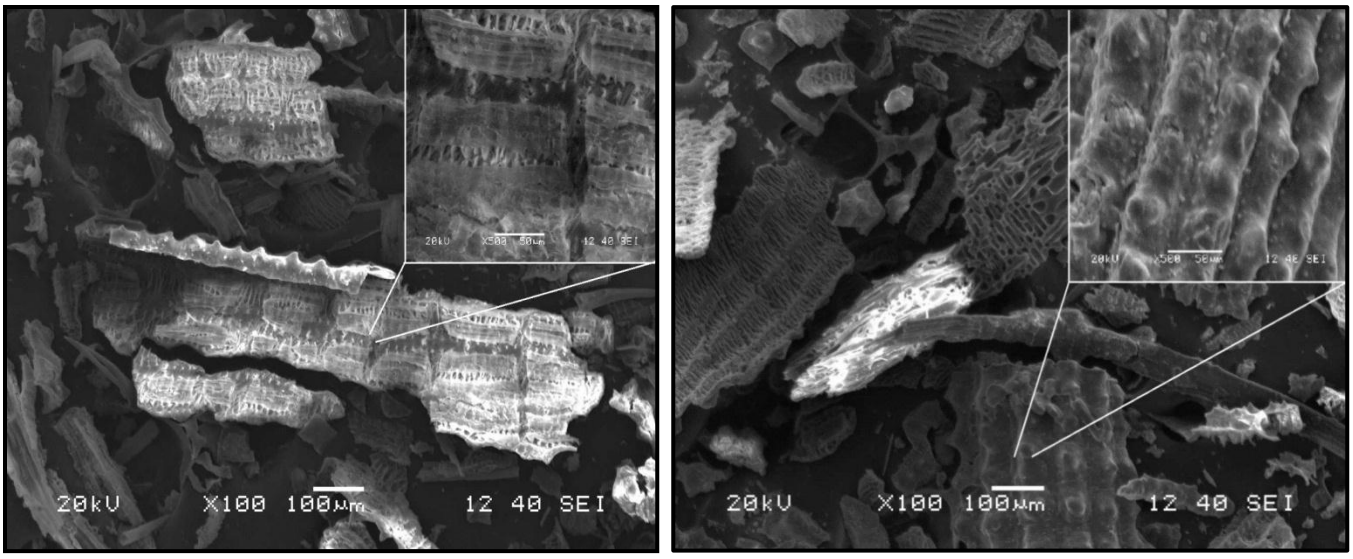

Fig 4.13, 4.14: FESEM image of RHA at 100x; inset: 500x(inner surface), FESEM image of outer surface (inset: with 500X magnification)

4.2.2 FESEM and EDX Analysis of Silica Derived from Pyrolysed RHA

The silica extracted from water washed rice husk, before pyrolysis were scanned under SEM and EDX spectra analysis were performed. Silica obtained from pyrolysis of water washed RHA at temperatures of 650^{o} C and 750^{o} C were performed. The SEM image of silica, pyrolysed at 650^{o} C, at 200x magnification and 500x magnification in the inset are shown in *Fig 4.15*. Particle sizes of about 10-100 µm were observed. The EDX study of the silica sample shows the presence of silicon, 94.28%, and oxygen in form of silica and Sodium, 2.26%, from the acid titration. *Fig 4.16* shows the SEM image of silica obtained from water washed rice husk pyrolysed at 750^{o}C. The image shows particles with size from 10-200 µm and EDX confirms the presence of silicon, 93.27%, in form of silica, sodium and also Nitrogen formed during titration of the silica from the sodium silicate solution. The percentage of silicon is seen to be little less than that in silica obtained from RHA pyrolysed at 650^{o} C, this might be attributed to the higher presence of Na and NO_3, which can be removed by washing the silica filtrate before drying.

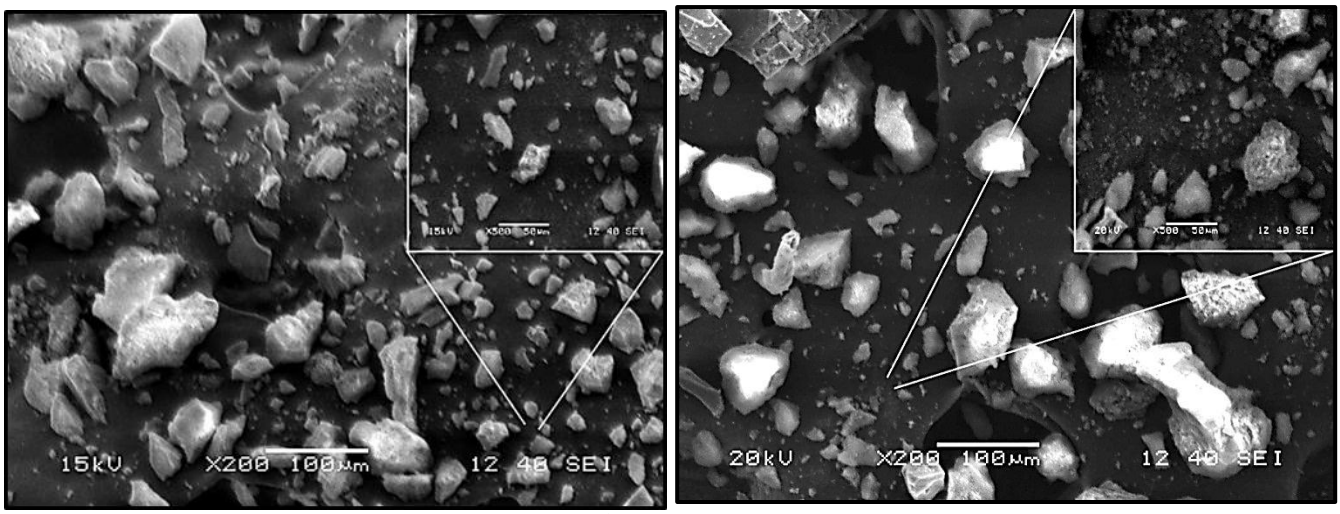

Fig 4.15, 4.16: FESEM image of silica (650^{o} C) at 100x; inset: 500x, and of Silica (obtained at 750^{o}C pyrolysis)

Similar to silica from RHA water washed prior to pyrolysis, silica obtained from RHA with prior acid wash with 1N HNO_3 was also tested under FESEM and corresponding EDX performed. FESEM images of silica obtained at 650^{o} C is shown in *Fig 4.17* and *4.18*. The silica particle sizes range from 20-200 µm as visible from the FESEM images. EDX analysis showed the presence of 96.99% silicon in form of SiO_2 and 1.56% and 0.75 % of Na and N respectively. FESEM analysis of silica extracted from RHA after pyrolysis at 750^{o} C with prior acid washing was also performed is also shown in Fig 6. Particle sizes range from 10-200 µm and EDX showed presence of 95.48% of silicon in form of SiO_2 and 2.54 and 1.98% of Na and N respectively.

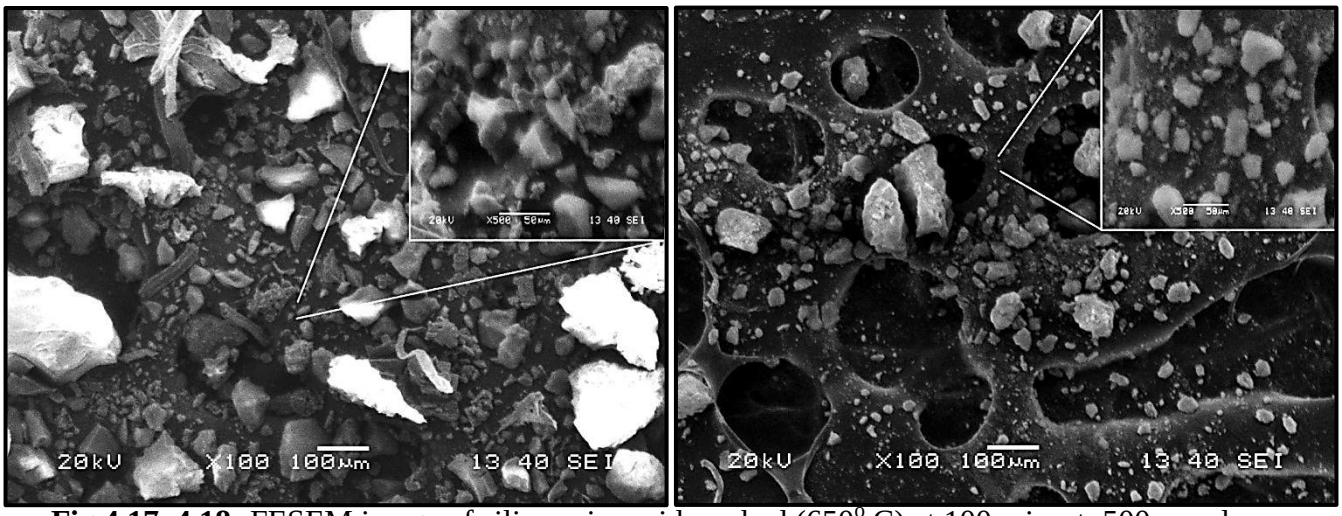

Fig 4.17, 4.18: FESEM image of silica-prior acid washed (650^{o} C) at 100x; inset: 500x, and Silica-acid washed(obtained from pyrolysis at 750^{o}C)

4.3. Nitrogen Sorption Analysis

4.3.1. N_2 Adsorption-Desorption of silica derived from RH

Silica was obtained from AW RhSi pyrolysed at temperatures of 650, 750, 850^{o}C were subjected to nitrogen adsorption and desorption tests. The multipoint BET curves indicating the isotherms are shown in *Fig. 4.19*. The isotherms were identified as type III indicating formation of multilayer and capillary condensation taking place in mesopores. A relative steep trend is shown for silica obtained at 750^{o}C due to formation of multilayer. Type III isotherm curves usually result from agglomerate particles or aggregates containing non-uniform pores. The surface area, total pore volume and pore diameter were calculated using BET model and the results for the silica obtained from RHA pyrolysed at different temperatures is tabulated in *Table 4.10*. It is observed that the surface area decreases with the increase of the pyrolysis temperature. The increase of temperature decreases the amorphous nature of the silica obtained the microporous nature slowly diminishes due to more formation of crystalline silica at elevated temperatures. A maximum surface area was obtained for silica derived from RhSi pyrolysed at 650^{o}C. Analysis of the adsorption characteristics using Density Functional Methods also generate similar results and are summarized in *Table 4.11*. Average pore diameter is found to be in the range of 2-3 micro meters proving that it is extremely mesoporous in nature. Silica obtained at lower temperatures was found to have lower pore diameter, in other words higher cumulative surface area and higher pore volume.

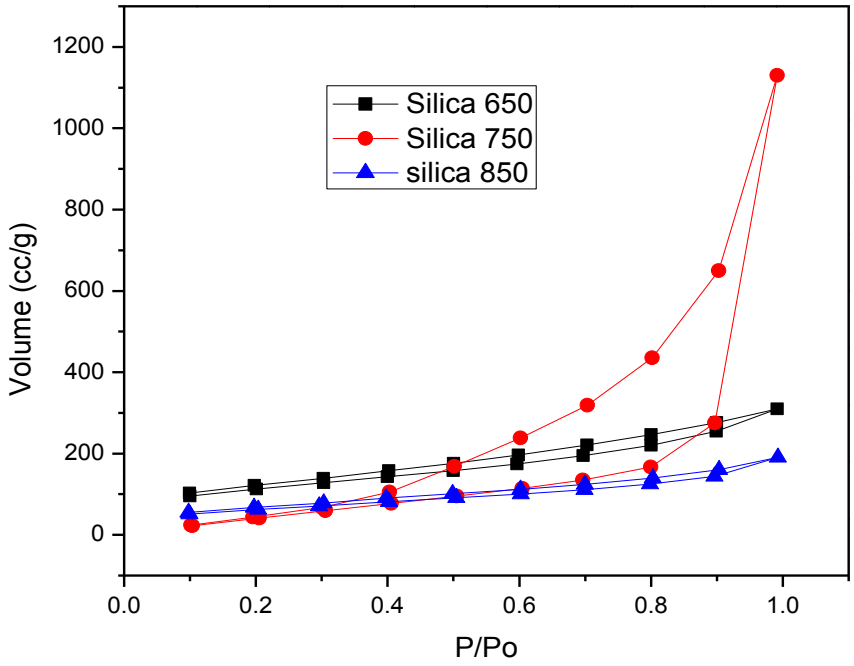

Figure 4.19: The N_2 Adsorprtion-Desorption analysis of Silica from RH at different temperatures

Table 4.10: The N_2 Adsorption-Desorption Analysis Parameters of Silica Based on BET Calculations

Type of Silica	BET surface area (m^2/g)	Pore volume (cc/g)
Silica (RhSi650^{o}C)	343.36	0.4796 for pores smaller than 225.9 nm
Silica (RhSi750^{o}C)	243.25	0.2943 for pores smaller than 256.4 nm
Silica (RhSi 850^{o}C)	119.56	0.1748 for pores smaller than 229.36 nm

Table 4.11: The nitrogen adsorption-desorption analysis parameters of silica based on DFT method pore size distribution calculations

Type of Silica	Cumuative surface area (m^2/g)	Pore volume (cc/g)	Average diameter (nm)
Silica (RhSi650^oC)	265.339	0.2794	201.95
Silica (RhSi750^oC)	145.923	0.196	276.78
Silica (RhSi850^oC)	110.064	0.1889	316.8

4.3.2. N_2 Adsorption-Desorption of metal Modified Silica Catalyst derived from RH

Fig. 4.20 shows the BET isotherms of Metal Modified Silica Catalyst extracted at pH of 10, 7 and 3. All the three catalysts exibit type II adsorption isotherm curves and thus prove its mesoporous. The volume of N_2 adsorbed for the catalyst extracted at lower pH is lower than that extracted at higher pH. The low specific surface area and low pore diameter in case of higher metal loading in comparision to the catalyst with lower metal loading, i.e higher pH causes the above. The isotherms of the catalysts extracted at the pH of 10, 7 and 3 have hysteresis loop. Presence of hysteresis loops suggests that a network of pores exist on the silica surface and bulk. They are supposed to have narrow openings and a larger pore with the matrix, typically looking like ink-bottle shaped pores. Nitrogen accumulates and gets adsorbed in the small pores and its narrow openings. During desorption the rate of desorption does not match the adsorption rate and volume and some residual gases remain blocked in the pores leading to the fact that the adsorption and desorption lines don't meet. Type H3 hysteresis loop was observed for all the samples indicating that the catalyst has a wide pore size distribution consisting of various sized pores and having aggregated or agglomerated particles with non-uniform size and shape. The N_2 sorption surface analysis parameters are presented in *Table 4.12*. A trend of decreasing surface area with increasing metal loading, i.e. decreasing pH, is

observed. This is due to more metal uptake by the silica during preparation using the sol-gel techniques. All the three catalysts have a wide pore size distribution, which is represented in *Table 4.13*. The cumulative surface area is seen to decrease with the reduction of pH, i.e. with increase of metal loading. The decrease is due to the deposition of Chromium and Copper species inside the pore orifice. Crystalline Cr_2O_3 and CuO/Cu_2O form on the catalyst surface which block away the pores on the silica surface.

The wide pore size distribution is due to the presence of nitrate and CrO_4^{2-}/Cr^{3+} ions along with Cu^{+}/Cu^{2+} ions. The hydrolysis and condensation process of the silicon precursors cause the wide pore size distribution. At high pH the base-catalysed hydrolysis and condensation process took place at a slower rate. In higher pH the presence of NO_3^- will block the adsorption of silicate ions on the micelles and delay the formation of silica/surfactant mesophases, which is also evident from the XRD data in the patter list of the compounds on the surface which decrease on increasing pH. Higher pH causes incomplete interaction between the surfactant and the silica in its ultimate form. Thus smaller pores are formed by the help of the template itself. Agglomeration of silica nanoparticles during the hydrolysis-condensation process aids in agglomeration of silica nano particles helping in the formation of larger pores . Likewise, the hydrolysis and condensation process takes place at a faster rate in acid medium. The condensation process usually speeds up in the presence of metal cations, but is not in this case, maybe due to the bulky chromium and copper complex ions which hinder the formation to siloxane groups, with the aid of nitrate ions, from silanol groups. Around the isoelectric point of around the pH of 2 the silica is almost chargeless, being unable to directly combine with positively charged surfactant (CTAB). This brings out the need for a bridge counterion at the silica-surfactant interface which is NO_3^- in this case. Bridging silica and the surfactant leads to a unimodal pore system, after completion of hydrolysis and condensation.

RhSi-Cr/Cu-10 was found to have a pore size in the range of 105 – 198 Å, RhSi-Cr/Cu-7 has a pore size range of 89 – 180 Åand RhSi-Cr/Cu-3 in the range of 62 – 155 Å. The incorporation of chromium and copper was found to close the smaller pores that existed in the RhSi-10 and Rhsi-7. The specific surface area of RhSi extracted at pH 7 for samples pyrolysed at 750^{o}C was 243.25 m^2/g which decreased, on incorporation of

chromium and copper, to 111.1 m^2/g. The amount of chromium and copper loaded had a direct influence for decreasing the surface area of the catalysts.

A Density Functional Theory analysis of the adsorption characteristics of the catalyst show an average pore dia in the range of 20 – 30 nm with an average pore volume of 0.2 – 0.3 cc/g. The cumulative surface area is seen as 202.41, 123.478 m^2/g and 96.762 m^2/g for RhSi-Cr/Cu-10, RhSi-Cr/Cu-7 and RhSi-Cr/Cu-3 respectively. The increase in pore diameter is due to more metal being impregnated into the pores and on the surface of the silica also leading to a decrease of the pore volume. Thus through this it can be expected that the reactivity of the catalyst with higher metal loading will decrease in comparision to the one with lower metal loading.

Table 4.12: The N_2 Adsorption-Desorption Analysis Parameters of Silica Catalyst based on BET Calculations

Type of Silica Catalyst	BET surface area (m^2/g)	Pore volume (cc/g)
RhSi-Cr/Cu-10	182.7	0.2798 for pores smaller than 197.35 nm
RhSi-Cr/Cu-7	111.1	0.2402 for pores smaller than 217.15 nm
RhSi-Cr/Cu-3	79.94	0.1943 for pores smaller than 235.23 nm

Table 4.13: The N_2 Adsorption-Desorption analysis parameters of silica catalyst based on DFT method pore size distribution calculations

Type of Silica Catalyst	Cumulative surface area (m^2/g)	Pore volume (cc/g)	Average diameter (nm)
RhSi-Cr/Cu-10	202.41	0.2904	2.1104
RhSi-Cr/Cu-7	123.478	0.2511	2.3425
RhSi-Cr/Cu-3	96.762	0.2041	2.6621

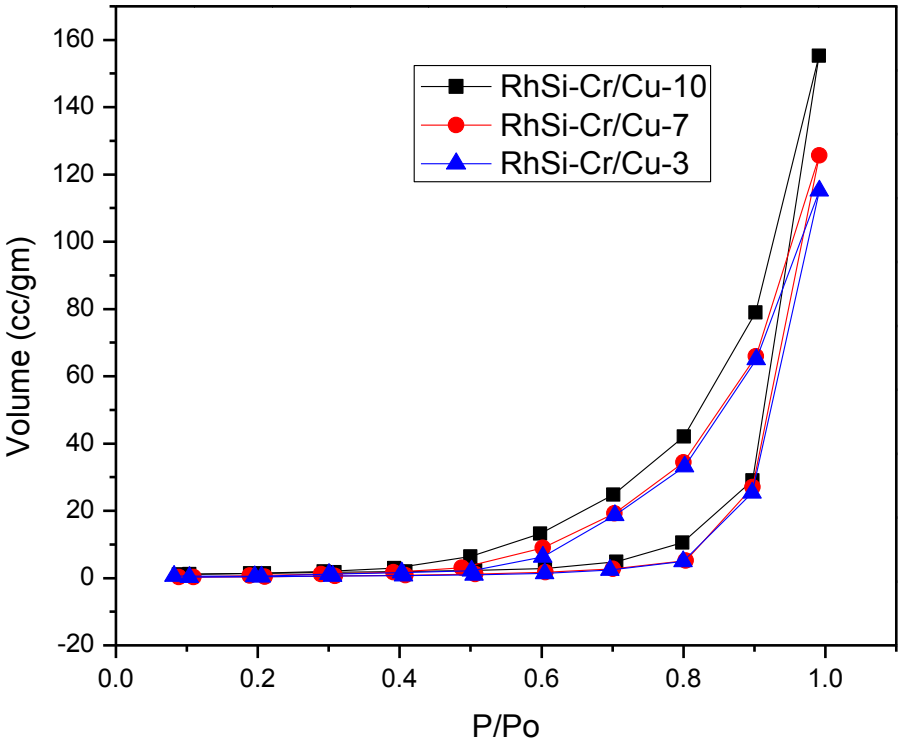

Figure 4.20: The N_2Adsorprtion-Desorption analysis of Metal Modified Silica Catalyst from RH extracted at different pH

4.4. Thermogravimetric Analysis

4.4.1. Thermogravimetric Analysis of Mesoporous Silica extracted from RH

The TGA curve of silica obtained from pyrolysis of AWRHA pyrolysed at 650,750 and 850^{o}C, i.e. RhSi 650, RhSi 750 and RhSi 850^{o}C, is shown in *Fig. 4.21*. TGA analysis was carried out at temperature range from room temperature to 1000^{o}C with a heating rate of 10^{o}C per min. The TG curves shows a four stage mass loss with a total mass loss of around 50% in average for silica from RhSi 650 and around 30% mass loss for silica obtained from rice husk pyrolysed at higher temperatures, i.e. RhSi 750 and RhSi 850. The silica lose mass only upto 20% upto a temperature range of 750-800^{o}C. The steps can be distinguished as 50-150, 150-350, 350-650 and 650-1000^{o}C which are also in parity with the TG analysis in literature. The initial decrease of mass is due to removal of moisture from the pores. Further mass loss is due to removal of moisture from

the meso and micro pores. The steep decrease in mass after around 750^{o}C is attributed to dehydroxylation of silanol. A greater mass loss is observed for silica obtained from rice husk pyrolysed at lower temperatures than silica obtained from rice husk pyrolysed at comparatively higher temperatures. A change of slope is also visible for samples pyrolysed at 850^{o}C. Thus this can be said that with the increase of temperature the mass loss due to heating above 750^{o}C increases. This is because with the rise of temperature during pyrolysis the silanol bonds already break down and form siloxane bonds which are much more difficult to disintegrate by application of heat. In other words we can also say that some amount of the amorphous silica changes its nature to crystalline form on heating above 800^{o}C forming crystoballite, which can be correlated with the XRD data proving the same, i.e. presence of crystalline nature in the silica above 800^{o}C.

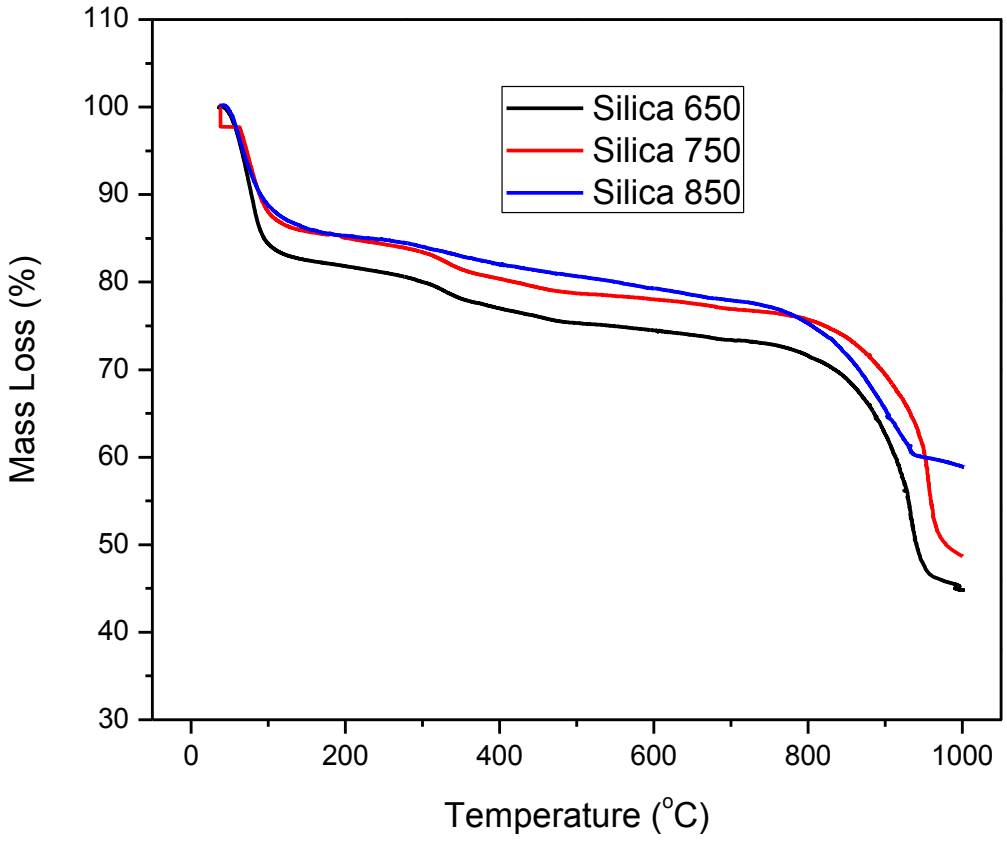

Figure 4.21: The TG curve of silica (different temps.)

4.5. FT-IR Analysis of silica catalyst

The FTIR spectra for RhSi-Cr/Cu-10, RhSi-Cr/Cu-7 and RhSi-Cr/Cu-3 are shown in *Fig 4.21.* A broad band at 3400 cm^{-1} is seen and reason to be formed by the stretching vibrations of the silanol (Si-O-H) bond and the H-O-H bonds of the water molecules. Bending mode vibrations of adsorbed water molecules causes the band around 1650 cm^{-1}. The intensity of this band is seen to decrease with the decrease of pH, indicating that the amount of H_2O adsorbed in the silica catalyst surface decreases with reduction of pH to the acidic end. The strong band around ca. 1700 cm^{-1} indicate asymmetric stretching vibrations of the structural siloxane (Si-O-Si) bond. This helps to confirm the presence of silica in the catalyst matrix. The band at ca. 802 – 807 cm^{-1} and 440 – 470 cm^{-1} is caused due to two different reasons, first being the symmetric stretching and the second as bending modes vibrations, of the bulk Siloxane (Si-O-Si) bonds present at all the samples. The presence of NO_3^- species, from the use of nitric acid during the acidification process, causes the presence of the sharp band at 1385 cm^{-1} , which has been also found

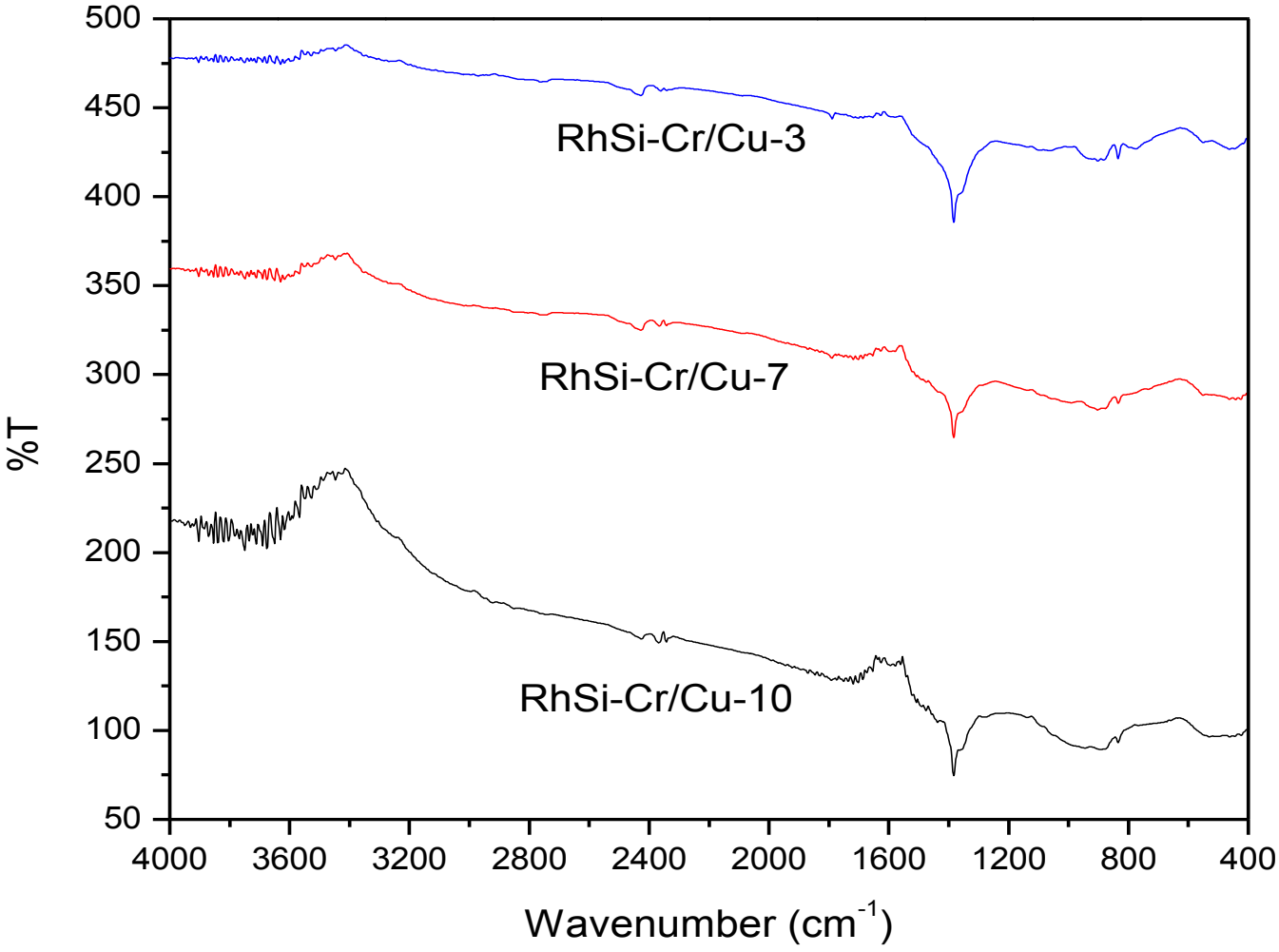

Fig 4.22: FT-IR spectra for the catalysts prepared at various pH

to be present in all samples.

Asymmetric stretching vibration of Si-O-Cr lead to the formation of several new bands at around 903 cm^{-1}. The bands at 834 cm^{-1} is due to the Si-O-Cu present on the silica surface depicted in *Fig 4.23*. This band is seen to become more sharp with the reduction of pH, indicating formation of more Cu^{+} instead of Cu^{2+} at lower pH, vice versa in case of the opposite, i.e. at lower pH. An increase of the Copper content loading on the silica matrix results in a much more sharp band at 834 cm^{-1} confirming this band is band is due to presence of Cu^{2+} on the surface. The presence of Cr-O-Cr of Cr_2O_3 moiety, formed during calcination, develop the band at 774 cm^{-1}. An increase in the Cu content in the catalyst also leads to the band at 1101 $cm^{-1}$to become prominent which is due to Cr and Cu forming complexes on the silica matrix and also the Si-O-Cu bonds becoming more active sites for oxidation. This band is almost not present on the samples extracted at the same pH of 10 for lower Copper loading samples.

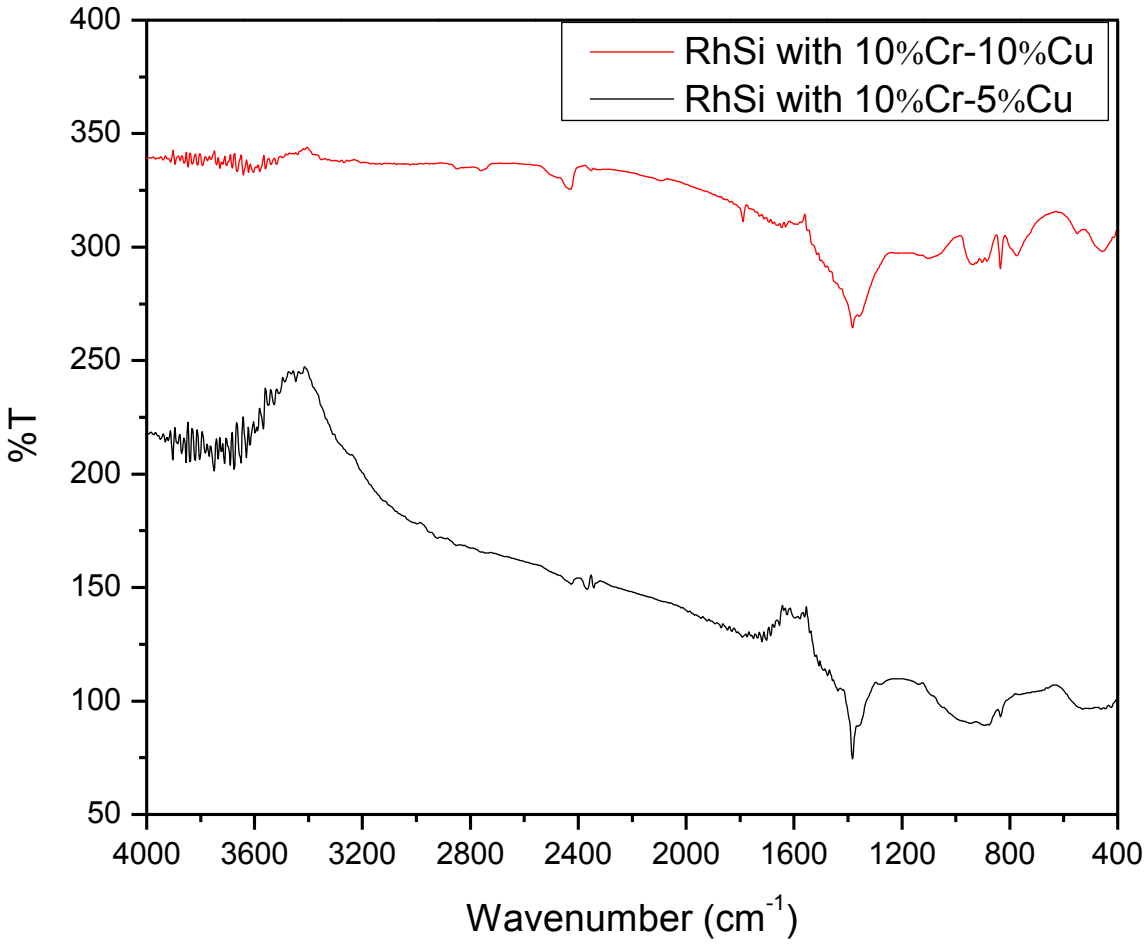

Fig 4.23: Comparision of FT-IR spectra of the catalysts with 10% Cu and 5% Cu loadings extracted at pH of 10

4.6. Oxidation of Styrene in the Liquid Phase.

The products were removed at intervals of one hour from the reaction vessel to which 1µl of m-xylene was added and the samples immediately injected into the GC-MS chamber. Benzaldehyde (Bhd) was the main product detected from GC and GC–MS. Other byproducts produced were phenylacetaldehyde (PhAhd), acetophenone (AcPh), phenylgloxal (PhGal) and benzoic acid (BzA). A maximum of 76.65% conversion of styrene is observed from *Table 4.14* for RhSi-Cr/Cu-3 while only 12.56% conversion of styrene is observed for RhSi-Cr/Cu-10. RhSi-Cr/Cu-7 managed a conversion of 43.41%. RhSi-Cr/Cu-10 and RhSi-Cr/Cu-7 have lesser surface area which. Thus the diffusion of reactants and the products in and out from the pores are hindered due to unavailability of surface pores. The amount of chromium and copper loaded rather than the pore size distribution or surface area of the catalysts causes its catalytic activity. This observation corresponds to other literature where chromium–silica or copper-silica catalysts have been used for other types of oxidation reactions using H_2O_2 as oxidant. Bhd was only found when RhSi-Cr/Cu-10 was used as the catalyst with selectivity of PhAhd and AcPh are slightly higher when RhSi-Cr/Cu-7 was used compared to RhSi-Cr/Cu-3. BzA selectivity was 3 times higher when RhSi-Cr/Cu-3 was used compared to RhSi-Cr/Cu-7. A greater amount of BzA is found when greater amount of chromium and copper active sites causes oxidation of Bhd to BzA. Due to the higher catalytic activity of RhSi-Cr/Cu-3 it was further used to evaluate other reaction parameters.

Table 4.14: The effect of preparation pH of catalyst on the product selectivity during oxidation of styrene

Catalyst	**Conversion (%)**	**Bhd (%)**	**PhAhd (%)**	**AcPh (%)**	**BzA (%)**
RhSi-Cr/Cu-10	12.56	99.84	0	0.16	0
RhSi-Cr/Cu-7	43.41	82.14	5.6	6.3	5.96
RhSi-Cr/Cu-3	76.65	79.42	4.4	4.09	12.09

Effect of metal loading, i.e increasing the amount of Copper ion the catalyst was also analysed. RhSi-Cr/Cu-3 having 10%Cr and 5% Cu and RhSi-Cr/Cu-3 having 10%Cr and 10%Cu were compared keeping all other parameters like H_2O_2 to styrene ratio, temperature of reaction and mass of catalyst used same is depicted in *Table 4.15*. Conversion percent is seen to further increase on increasing copper loading content with increase in Bza selectivity too. Acetophenone and benzoic acid selectivity is also found to decrease. Overall More copper loading has given better conversion and also better selectivity to benzaldehyde and also reduced undesired products.

Table 4.15: The effect of copper loading in the catalyst on the product selectivity.

Catalyst	**Conversion (%)**	**Bhd (%)**	**PhAhd (%)**	**AcPh (%)**	**BzA (%)**
RhSi-Cr/Cu-3, 5% Cu	76.65	79.42	4.4	4.09	12.09
RhSi-Cr/Cu-3, 10% Cu	89.41	82.13	3.6	3.26	11.01

CHAPTER 5

EPILOGUE

5.1 Conclusions

This study revealed the process for extraction of silica from rice husk and also primarily in amorphous form. The removal of the mineral and organic component from the rice husk helped to obtain high yields of silica from the ash. All existing techniques for obtaining silica are primarily operated at temperatures of around 1500^{o} C, while this process used in this work has been made possible in a temperature range of 550-750^{o} C. This proves to be highly energy efficient and also a useful technique for waste disposal and utilization. For cases where even pyrolysis was performed the temperature use was far less than the conventional techniques.

The initial acid washing of the rice husk prior to pyrolysis have shown to improve the quality of the silica and eliminate trace of other organic and inorganic elements. This silica derived can be further used as catalyst framework and can be impregnated with heavy metals to act as catalyst itself. The surface area and adsorption isotherms can be calculated and proper catalyst can be obtained from it. The white silica was proved amorphous by the XRD studies and a proper comparison was made between various samples showing the effect of variation of temperature and pyrolysis conditions. Hence, production of value added materials from rice husk not only facilitates utilization of an abundantly available agro-waste but also reduces environmental pollution.

The surface area was found to be in the microporous range and having a high surface area, thus they can be used as adsorbents or as catalyst framework. The high surface area of the silica will provide as sites for active reactions and charge transfer to facilitate high rates of reactions. Oxidation reaction can be undertaken and effect of this developed catalyst can be studied. Performance of such catalyst over catalyst of copper made on commercial MCM can also be compared. The conversion percentage of styrene to benzaldehyde has been compared with heterogeneous catalysts of chromium and copper alone respectively.

The incorporation of bimetals into the silica matrix has helped to further increase product conversion and selectivity to benzaldehyde with considerable reduction in byproduct formation. The effects of metal loading on the catalytic activity of the catalyst for benzaldehyde conversion and also on the total conversion to product has also been studied. An increase of the amount of copper loading onto the silica matrix during the

sol-gel extraction helped to increase the oxidation capacity of the catalyst. The effect of pH of extraction of the silica catalyst were also studied and found out that the maximum conversion is archived for metal modified silica catalyst extracted at lower pH, i.e. at acidic medium. Though the surface area of the catalyst extracted at lower pH had relatively low surface area and low pore volume, yet they were found to be more efficient for styrene conversion and product selectivity, which can be attributed to the copper and chromium present on the surface. The comparison of the catalytic activities of the high surface area catalysts at different pH levels were found to be excellent for oxidation of styrene high benzaldehyde selectivity. Presence of high surface area helps more active suites to be available on the silica surface which accounts for the general better performance of all the metal modified catalysts developed here. Also it can be said the catalytic activity is not only due to the high surface area of the catalyst but also due to other factors.

5.2. Future scope

The oxidation states and the silica-metal bond on the surface can be identified using UV-Vis diffuse reflectance techniques. Such a study can help to identify the exact reaction mechanism followed and the route to formation of benzaldehyde from styrene and also the cause of formation of intermediates and byproducts. Effect of pyrolysis temperature and effect of concentration of metal ions, effect of aging the precipitate, effect of calcining the dried catalyst, SDA concentration can be checked to obtain best possible method to prepare the catalyst. The reusability of the catalyst can also be checked. Styrene can be a common substance which can be chosen to be oxidized in presence of an oxidizing agent like H_2O_2. The effect of use of different weight of catalyst, varying the recation time and the temperature, styrene to H_2O_2 ratio in the conversion percentage to benzaldehyde and conversion to product can be analyzed. Characterization techniques like ICP and NMR can be used to identify the exact surface bonds and oxidation states.

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